LUMINESCENT SUBSTANCES

by F. A. KRÖGER.   335.37

On the basis of the atomic theory a concept is developed of the mechanism of the fluorescence and phosphorescence of the luminescent substances commonly used in technology, such as zinc sulphide, willemite, calcium and magnesium tungstate, cadmium borate, etc. Especial attention is paid to the energy levels of the electrons in a solid luminescent substance and their relation to emission and absorption phenomena.

Introduction

At the present time a large number of luminescent substances are known. These are substances with whose help it is possible to convert corpuscular radiation, X-radiation or ultra violet radiation into light, or in general into a form of radiation which is different from the original form.

To begin with a simple example of the application of such substances we may refer to the luminous dials of watches which are covered with a preparation which contains in addition to the luminescent substance a very small amount of a radioactive element (radium or mesothorium). The latter elements emit alpha particles of high energy which cause the luminescence of the preparation.

A second example is formed by the screens which are used in fluoroscopy with X-rays. The screens have the property of emitting intense light under the influence of X-radiation, so that the shadow picture thrown by the X-rays on the screen becomes visible to the eye. A related application is formed by the reinforcing screens for X-rays which produce photographically active light, so that a more intense image is formed than upon direct action of the X-rays alone.

The conversion of electron rays into light is encountered in the case of the substances from which the screens of cathode ray oscillographs and television tubes are made. Finally, the conversion of ultra violet radiation into light takes place in modern gas-discharge lamps (luminescence lamps).

Fluorescence and phosphorescence

The conversion of electromagnetic (especially ultra violet) radiation into light of another wave length, namely into visible light, is called fluorescence [1]. In addition to the phenomenon of fluorescence, many fluorescent substances exhibit a second peculiarity, namely a very long afterluminescence (very familiar at present in the case of the luminescent buttons and pins which are worn during the blackout). This phenomenon, phosphorescence [2]), is distinguished from fluorescence by its great dependence on temperature. If a luminescent button, after having been irradiated, is immersed, in the dark, in a glass of hot water, it suddenly gives much light, which, however, rapidly decreases in intensity. Conversely, a low temperature has a retarding action on the giving off of the energy, so that the luminescence lasts longer when it is cold. At a very low temperature (immersion in liquid air) the luminescence disappears entirely; the energy absorbed can then be stored for an almost unlimited time and whenever desired it can be produced again by heating. The mechanism of phosphorescence is closely connected with that of fluorescence, but it must be considered separately. A single word which is used to indicate both the phenomena is luminescence. For that reason the fluorescent and phosphorescent substances used in technology, especially when the phosphorescence is only a subsidiary property, are often called luminophors.

On previous occasions the phenomenon of

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[1]) From the mineral fluor-spar or fluorite (CaF_2) which in the presence of certain admixtures, such as some of the rare earths, clearly shows the phenomenon.

[2]) Phosphor = light bearer, is the name of these preparations originating about the year 1600, which then first became known in Europe.

fluorescence has been studied in some detail in this periodical, gases and liquids as well as solid substances were then discussed. In this article we shall go somewhat more deeply into the luminescence of solid substances. We shall discuss, in addition to the chemical composition, the mechanism of light emission in the case of free atoms and crystals, the absorption spectrum of the substances in question, the connection between absorption of light and fluorescence, and, further in particular the influence of small amounts of foreign substances on absorption and emission.

Chemical composition

Luminescent substances of very divergent chemical composition are known. Certain substances (salts of rare earths, uranyl salts, benzene) possess the property of luminescence in the pure, unmixed state. In other cases the phenomenon only becomes intense when the substance in question is present as a slight admixture in another substance. Ruby is an example of this. Lecocq de Boisbaudran (1886) showed that Cr_2O_3 as an admixture in the basic material Al_2O_3 is the active component. A second example of an admixture phosphor, which also exhibits a strong phosphorescence, is CaS. This compound forms the chief component of the luminescent paint whose luminescence was shown by Verneuil (also in 1886) to be due to extremely small traces of bismuth (Bi_2S_3). In the same year E. Becquerel discovered that calcite ($CaCO_3$) only exhibits luminescence in the presence of small amounts of manganese (Mn). Becquerel and Lenard (1890) carefully examined the properties of such preparations.

In addition to the above-mentioned compounds of rare earths a number of other substances are known which are luminescent even when no foreign substances are present. These are substances in which a deviation from the stoichiometric chemical composition is the condition for the appearance of the phenomenon. Thus ZnS and ZnO are luminescent when a small excess of Zn-atoms is present in the lattice. Somewhat similar cases are those of $ZnCO_3$ and $CaHPO_4$, where it is known that they only exhibit luminescence in a partially decomposed state.

The mechanism of the emission of light

According to the quantum theory a system of electrons, such as occurs in the case of an atom, molecule or crystal lattice, can only exist in discrete states, each of which is distinguished by a definite energy content. We thus distinguish the following energy states: E_0, E_1, E_2, etc. The state with the lowest energy (E_0) is called the basic or normal state. When the system is in a state of higher energy (also called an excited state) in many cases it returns spontaneously to a lower state, emitting as it does so a quantity of light (light quantum) such that Bohr's (1913) equation is satisfied:

$$E_2 - E_1 = h\nu_e.$$

In this equation ν_e represents the frequency of the light emitted (in sec.$^{-1}$), while h is a constant ($h = 6.6 \times 10^{-27}$ erg sec.). If the energy is measured, as is often done, in electron volts instead of ergs (1 eV $= 4.8 \times 10^{-10} \times 1/300 = 1.6 \times 10^{-12}$ ergs) and if, instead of the frequency, the number of wave lengths per cm (ν_{cm}^{-1}) or the wave length λ in Å is used, then

$$(E_2 - E_1)_{eV} = 8072\ \nu_{cm^{-1}}$$
$$(E_2 - E_1)_{eV}\lambda_Å = 12\,390.$$

In general it is possible to bring a system into a higher state of energy by irradiating it with corpuscular rays or with light. In the latter case the following condition must be exactly satisfied:

$$E_a - E_0 = h\nu_a,$$

where E_0 represents the energy of the basic state and E_a that of the excited state. ν_a is the frequency of the light which causes the excitation.

If the system is brought into the excited state by corpuscular rays (charged particles) the following less stringent condition is then in general valid:

$$\tfrac{1}{2}\ mv^2 \geqslant E_a - E_0,$$

where $\tfrac{1}{2}\ mv^2$ is the kinetic energy of the particle of mass m and velocity v.

If the system being considered is a free atom or molecule, E_a simply represents one of the states in which one of the electrons is displaced to an orbit with a higher energy. In the case of a crystal which is excited by light the same is true.

If excitation is effected by corpuscular rays (cathode rays, α-particles, electrons freed by X-rays) it must, however, be supposed that with the retardation in the crystal a single incident particle causes a large number of electrons to shift to higher orbits.

The process of emission is the same in both cases. For the sake of simplicity we shall in the following discuss only the luminescence caused by the absorption of light.

Some remarks on atomic structure

According to modern conceptions an atom consists of a positive nucleus surrounded by a more or less spherical swarm or cloud of electrons. According to the original concept of B o h r, neglecting the changes which the quantum theory has undergone since 1925 (wave mechanics), each electron describes a definite orbit. As an example in *fig. 1*
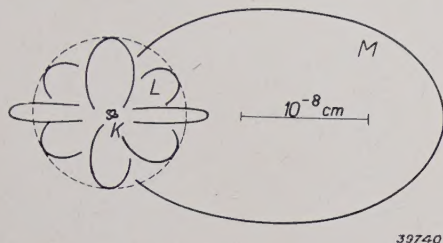

Fig. 1. Diagram of a sodium atom with its electron orbits according to B o h r's theory (from the year 1915).

a representation of a sodium atom according to B o h r's theory is given [3]). Each type of orbit can be traced by only a limited number of electrons (P a u l i principle). Some orbits remain very close to the nucleus. These thus contain strongly bound electrons. Other electrons move farther away from the nucleus and are thus less strongly bound. The orbits can be classified into shells. The K, L, M, etc. shells can be distinguished, with the strength of bond decreasing in this order, so that the K-electrons are more strongly bound than the L-electrons, the latter more strongly than the M-electrons, etc. The maximum occupation of the shells is:

K	L	M	N
2	8	18	32

According to the nature of the distribution of the electrons over the orbits the atom may exist in different states of energy, as indicated above. It is now found to be permissible to a certain extent to state that each electron moves in the average electric field of the nucleus and of all the other electrons together. One may therefore speak of the energy (sum of potential and kinetic energy) of one electron in its orbit, and the question may be put as to the magnitude of this energy. An estimation of this can be obtained from the so-called ionization voltages, which are the amounts of energy, expressed in eV, which are necessary to remove one electron from the atom. These energies can be determined by the methods of ordinary

spectroscopy and X-ray spectroscopy or with the electron impact method (F r a n c k and H e r t z 1914). In the case of sodium, for example, the following results are obtained.

The sodium atom contains a nucleus with the charge $+ 11e$ (e = charge on an electron = 4.8×10^{-10} e.s.u.) and 11 electrons. Two of these are bound in the K-shell with an energy of about 1000 eV, 8 in the L-shell with about 30 eV and 1 in the M-shell with about 5 eV. The further possible M-orbits and all N and higher orbits are empty in the normal sodium atom. It is found to be possible under the influence of light absorption or collision with a foreign particle that one of the electrons may leave its normal orbit and go into one of the unoccupied orbits or be removed from the atom. Thus for example the sodium atom may be in a state in which the M-electron travels in an orbit which, from the point of view of energy, is about 2 volts higher than the orbit in which it normally moves. In *fig. 2* the energies of the different electron orbits of sodium are given schematically, and in *fig. 3* the energy states of the atom considered
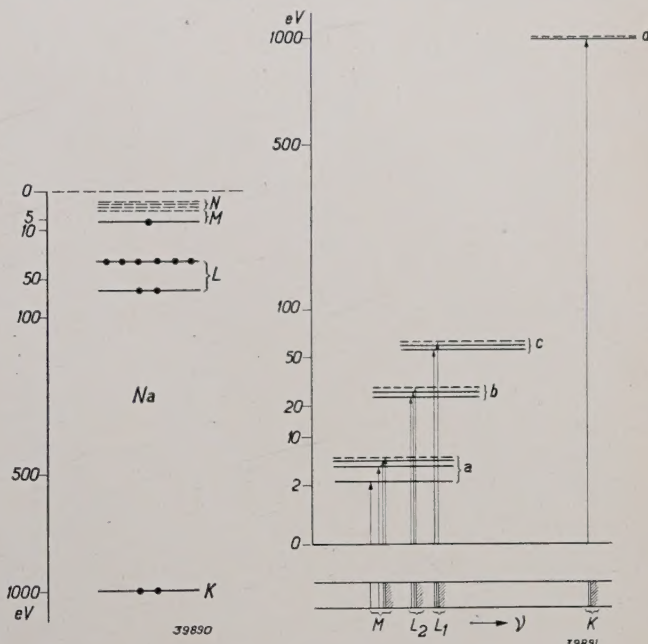

Fig. 2   **Fig. 3**

Fig. 2. Energies of the occupied (full lines) and unoccupied (broken lines) electron orbits in the sodium atom. In each case as zero point the state is chosen in which the electron is at rest at an infinite distance from the atom.

Fig. 3. Energy states of the sodium atom which result from the displacement of one of the electrons to orbits with higher energy. (The ordinate is drawn proportional to the square root of the energy).

States *a* result from a displacement of the M-electron, *b* and *c* result from excitation of one of the L-electrons, respectively, and *d* from excitation of a K-electron. As zero level the energy is chosen of the basic state of the atom given in fig. 2. Below may be seen a schematic representation of the absorption spectrum (on a non-linear scale).

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[3]) Taken with slight alterations from: H. A. K r a m e r s and H e l g e H o l s t, B o h r s atomtheori, Copenhagen 1915. The figure is slightly modified in accordance with the improvements which were introduced in the theory by P a u l i, S t o n e r and H u n d.

as a whole, which occur when one of the electrons passes from its original orbit to one of the unoccupied orbits whose energies are indicated in fig. 2 by dotted lines. Such transitions caused by absorption of radiation (light or X-rays) are indicated by arrows. The absorption spectrum is shown below the diagram of energy levels. This spectrum consists of a number of groups of lines which converge toward a limiting frequency which forms the beginning of a region of continuous absorption (absorption edge).

In addition to relatively simple cases like that of sodium there are also more complicated ones. In fig. 2 it was indicated without further remark that the L-shell contains two groups of orbits with different energies. The complete M-shell contains 3 subgroups, the complete N-shell 4 subgroups, etc. The maximum occupation of these subgroups by electrons is the same for each shell, beginning with the lowest it is always 2, 6, 10, 14 . . . . . Let us now take as an example of a complicated case the triply ionized atom of chromium (Cr^{3+}) which causes the luminescence of ruby. In the case of this ion the K and L-shells are completely occupied by electrons, likewise the first two subgroups of the M-shell. The third subgroup, however, has only 3 of the 10 electrons which it should contain at the

maximum. In *fig. 4* this state is shown as nearly as possible to scale.

The chromium ion can also pass into an excited state in which the energy content is greater than normal. Disregarding X-ray absorption, this may happen in the first place due to the fact that one of the most weakly bound electrons of the M-shell moves to an unoccupied higher orbit (for instance an N-orbit). There are, however, also states with an energy content greater than normal which occur due to the fact that the 3 electrons in the most weakly bound M-orbits are relatively differently grouped as regards their manner of movement. In *fig. 5* a number of these energy states of the chromium ion are represented: at *a* the states which occur by regrouping in the M-shell and at *b* the states which occur when an electron from the M-shell is brought into an N-orbit. Since such energy states often lead to absorption in the visible region of the spectrum, the ions with incompletely occupied subgroups are also called coloured ions.

Energy states of crystals

The state which exists in a crystal whose components (atoms or ions) are regularly arranged at distances of about 10^{-8} cm apart can best be approached by beginning with a sort of expanded crystal lattice in which the components are already placed according to the symmetry of the crystal in question, but in which the distances are so great that the ions or atoms do not yet affect each other. Let us examine for instance the energy scheme for a crystal which is built up of univalent positive ions A^+ and univalent negative ions B^-. For the energies of the individual electron orbits the considerations of the preceding section then hold. In addition to transitions of an electron to a higher orbit within the same ion, transitions can now also be imagined in which an electron passes from one ion to another. The charges of the ions involved are thereby changed. For example a positive ion A^+ which receives an electron becomes a neutral atom A, a negative ion B^- upon taking up an electron becomes a doubly charged ion B^{2-}. If we wish to represent these transitions in a scheme of electron energies, then in addition to the electron states of the ions A^+ and B^- we must also include those of A^+ and B^{2-}. This has been done in *fig. 6a* in which, however, representation to scale has not been considered and no particular ions were in mind.

Fig. 4. Energies of the electron orbits in the triply ionized chromium atom.

Fig. 5. Energy states of Cr^{3+} (non-linear scale).
a states occurring due to the regrouping of M-electrons,
b states occurring due to displacement of an M-electron to an N-orbit.
c ionization limit of the M-electron.
States which occur due to the displacement of an L or K-electron are not indicated. Below the energy scheme is the corresponding absorption spectrum (schematic).

The position of each level is determined by the energy which is necessary to bring an electron from the level in question of an atom or ion to infinity. In connection with this definition, in the indication of a transition between two levels the nomenclature of the level which gives up the electron
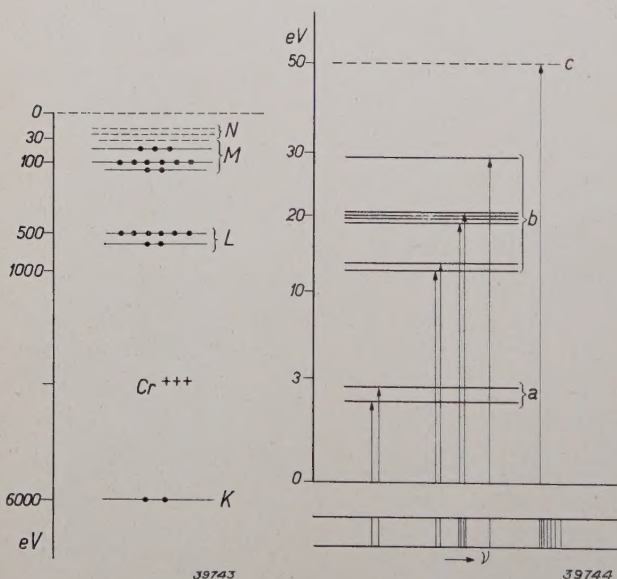
offers no difficulty. If, however, the electron is taken up by an ion (A+ for instance), we must give to the unoccupied level in question of this ion the name of the neutral atom formed (A). By definition the position of this is given by the energy which is necessary to take an electron from this neutral atom to infinity. This is, however, just the opposite of the energy which is r e c e i v e d when we make an atom out of the ion by adding an electron. The transition of an electron from an ion B− to an ion A+ is thus given in the energy scheme by the transition from the level B− to the level A.
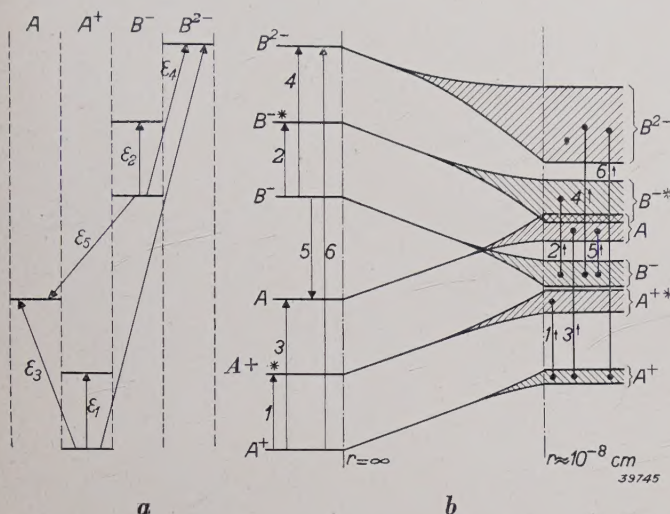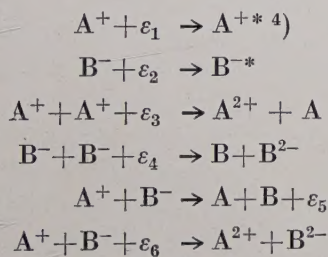

Fig. 6. Scheme of the possible energy states of the most weakly bound electrons of a positive ion A+, a neutral atom A and negative ions B− and B²− : a) in the free state, b) combined to form a crystal.

Possible transitions between the levels of fig. 6 are:

$$A^+ + \varepsilon_1 \rightarrow A^{+*} \; ^4)$$
$$B^- + \varepsilon_2 \rightarrow B^{-*}$$
$$A^+ + A^+ + \varepsilon_3 \rightarrow A^{2+} + A$$
$$B^- + B^- + \varepsilon_4 \rightarrow B + B^{2-}$$
$$A^+ + B^- \rightarrow A + B + \varepsilon_5$$
$$A^+ + B^- + \varepsilon_6 \rightarrow A^{2+} + B^{2-}$$

It will be seen that in the fifth process energy is l i b e r a t e d. This shows clearly that positive and negative ions are not stable side by side if there is no interaction between them. This may be understood when it is kept in mind that the formation of a positive ion from a neutral atom usually requires more energy, than is liberated when an electron is added to a neutral atom forming a negative ion (there are many cases indeed in which this latter process also requires energy!).

Let us now allow the ions of the expanded lattice to approach each other until a crystal is formed in which the ions are at normal distances apart (about 10^{-8} cm). Between the ions electrostatic

forces of attraction then begin to act. In the final state, the normal crystal, every positive ion is surrounded by a number of negative ions (in NaCl the number is 6), and every negative ion by a number of positive ions. At a greater distance there are indeed ions of the same sign as the ion under consideration, but the result will nevertheless be that the potential energy of the electrons at the position of a positive ion has risen and at the position of a negative ion it has fallen. As a result of this in our diagram the electron energy levels of A must rise compared with those of B−, and by an amount of the order of magnitude of 10 eV. This is shown schematically in fig. 6b. It will be seen that due to the mutual attraction of the ions the level B− is now below A ⁵).

In addition to the change in relative position of the levels, a second effect is also indicated in fig. 6b, namely a broadening of the levels. This effect is of a more complicated nature and was only explained by the modern atomic theory (wave mechanics). It is connected with the fact that upon approach of the ions the electron orbits partially overlap. Each level thereby splits up into a very large number of sublevels, namely as many as there are ions of the same kind in the crystal. Each sublevel can in general only be occupied by two electrons at the most. The collection of all sublevels belonging together which have been formed from one atom level is called an energy b a n d. From what has been said about the cause of the broadening it also follows that it will be greatest for those electron levels for which the corresponding orbits extend farthest outside the ion. The levels of the most strongly bound electrons, which remain very close to the nucleus, are thus only slightly broadened. The same is true for the more weakly bound electrons if the shape of the orbit is of such a nature that the electron does not move especially far outside of the circumference of the ion. This is the case for example for the most weakly bound M-electrons of the Cr^{3+} ion discussed above, and for the most weakly bound N-electrons of the rare earth atoms. If these atoms are of the coloured type, in which different energy states are possible due to different orientations of the orbits of the M or N-electrons, with respect to each other or to the orbits of the remaining electrons, the situation is one in which the

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⁴) An asterisk here indicates an e x c i t e d atom or ion.

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⁵) The figure is only a sketch and therefore more or less arbitrary. There are indeed cases in which the "crossing" of A and B− would not take place. This means that the starting point was wrong and that one was not dealing with an ionic crystal but with a crystal lattice which consists of atoms which attract each other by so-called homopolar binding forces.

transitions between these energy states take place as it were inside the atom (ion) without the whole crystal as such taking part. In *fig. 7a* the system of electron levels is given schematically for the combination: coloured positive ions and non-coloured negative ions, and in fig. 7b the energy band system of a crystal built up of these ions. Negative coloured ions also exist (NO_3^-). In general in this case the isolation of the electron orbits in question is less pronounced, so that the energy levels are broadened into bands.
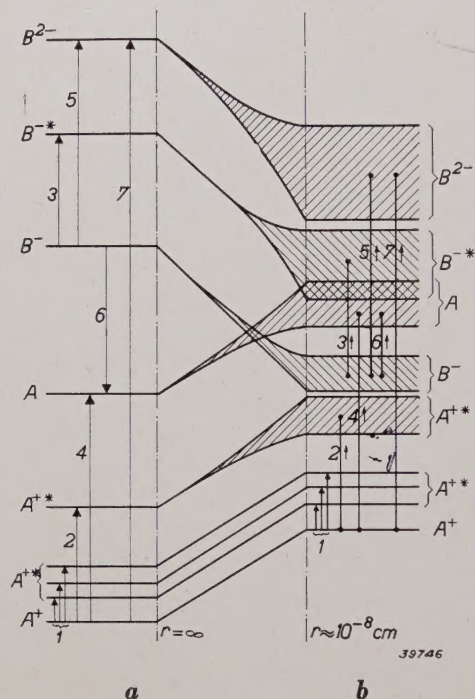

Fig. 7. Like fig. 6, but for the case in which the ions A+ are "coloured" ions.

Absorption spectrum of crystals

When a crystal is irradiated with light, then, analogous to what we have seen in the case of atoms and ions, absorption will only take place when the size of the quantum $h\nu$ corresponds to the energy difference between an occupied and an unoccupied band.

Since the position of the bands depends upon the nature of the ions, the crystal structure and the nature of the crystal lattice, these factors will also determine which transitions require the least energy.

In a normal ionic crystal the absorption spectrum will usually have the appearance of that sketched in *fig. 8* (corresponding to the case of fig. 6). The lowest absorption frequency here corresponds to the transition indicated by *5* of an electron from the band of the negative ions to that of the positive

ions. All the other absorption bands lie at higher frequencies, more or less overlapping.
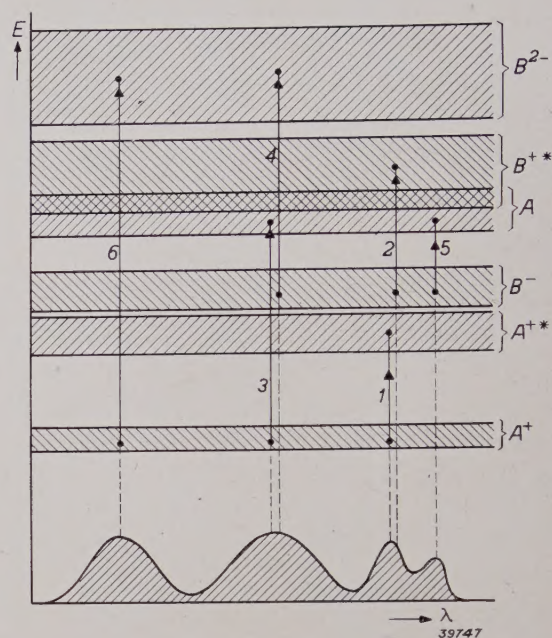

Fig. 8. Energy bands of the electron states of the crystal of fig. 6, with the absorption spectrum below.

For a crystal among whose components are coloured ions, the absorption spectrum is given in *fig. 9* (corresponding to fig. 7). In addition to broad absorption bands for which it is assumed that the band with the lowest frequency again corresponds to the transition from B^- to A^+ (with the formation of A), we now also encounter more or less sharp absorption lines, which are the result of internal transitions in the coloured ions. In the
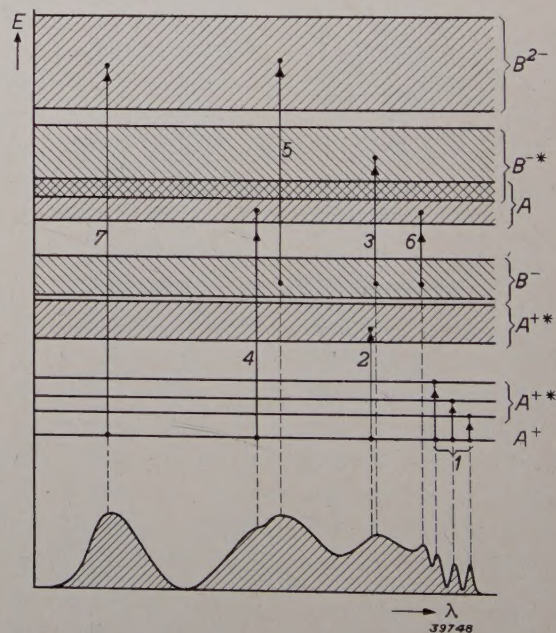

Fig. 9. Energy bands and absorption spectrum of a crystal with "coloured" positive ions.

scheme of fig. 9 it is assumed that these absorption lines lie at the long-wave edge of the crystal absorption bands (this is the case with most salts of the rare earths, e.g. $SmCl_3$). It will be clear that it need not always be so. In those cases, however, where the sharp absorption lines of the ions fall in the region of crystal absorption they cannot of course be observed. In the case of coloured negative ions also separate absorption bands of these ions are often observed at the long-wave end of the spectrum. Thus $CaWO_4$ and $NaNO_3$ exhibit absorption bands in the near ultra violet, which are to be ascribed to electron transitions within the WO_4^{2-} and NO_3^- groups, respectively, while the real crystal absorption bands of these crystals lie in the short-wave ultra violet.

Electron energies and absorption of disturbed crystals

As we saw at the beginning, in many cases luminescence occurs in connection with the defects in a crystal due to deviations from the stoichiometrical composition (unoccupied ion positions in the lattice and therefore local excess of the other kind of ion), or due to the fact that foreign ions are included in the lattice. The latter may occur in two different ways, namely:

a) due to the fact that foreign ions have taken the places of ions of the basic material (examples: ZnS in which Zn-ions are to a small extent replaced by Mn [6]) and Al_2O_3 in which several Cr-ions have occupied the positions of Al;

b) due to the fact that foreign ions have penetrated between the ions of the lattice (situated at so-called inter-lattice points; an example of this is ZnS to which a small quantity of Cu or Ag is added).

As a result of one of these two causes the energy bands in the immediate neighbourhood of these disturbed spots may undergo displacements as indicated in *fig. 10a*. As to the magnitude of these displacements, *i.e.* the local position of the energy levels with respect to the general band scheme, few prophecies can be made. We can, however, be certain in advance that we will obtain evidence of these extra levels only when they lie between the highest occupied band and the lowest unoccupied band of the undisturbed crystal, such as the occupied level D and the unoccupied level F in *fig. 10a*. In this case they may lead to transitions such as are

indicated by *2* and *3* in *fig. 10a*. These transitions are observed in the absorption spectrum as an extension of the crystal absorption (transition *1* in *fig. 10a*) toward the long-wave end.
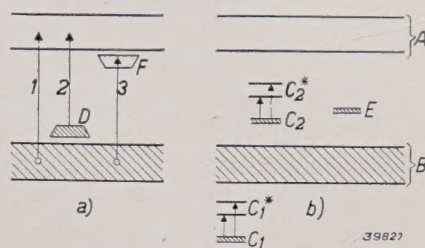

Fig. 10. *a)* Disturbance of the occupied and the unoccupied band, *1* crystal absorption, *2* transition from an occupied disturbance level to the empty lattice band, *3* transition from the full lattice band to an empty disturbance level.

b) Possible positions of the electron levels of built-in coloured and non-coloured ions. C_1, C_2 coloured ions, E non-coloured ions.

The foreign ions introduced or the excess ions present are also bearers of electrons which may again exist in different states to which (local) energy levels correspond. It is also impossible to say much in general about the position of these levels. It is, however, certain that the lowest occupied level must lie below the lowest unoccupied energy band of the crystal, since otherwise an electron would spontaneously pass from the foreign ion to the unoccupied band with the formation of a more highly ionized ion. If it is a question of foreign coloured ions, then in addition to the basic level and at a relatively small distance from it, other levels may occur corresponding to differently oriented orbits or to orbits of smaller bond energy, in the way discussed above for the case of Cr^{3+}.

In fig. 10b two possible positions of the energy levels for a foreign coloured ion are indicated by C_1 and C_2, and a possible position of a level of a non-coloured ion by E. In the qualitative consideration of the energy levels of foreign ions it makes little difference actually whether they form part of the regular lattice or have found a place in the inter-lattice points of the cristal or where the regularity of the crystal was already disturbed. Quantitatively there may be differences (height and relative position of levels) which we shall not go into here. If, as indicated in fig. 10b by C_1 and C_2, the distance between the levels of the foreign ion is smaller than the smallest distance between an empty and an occupied crystal band, more or less sharp absorption bands of the foreign ion can be observed at the long-wave end of the crystal absorption spectrum, just as in the case of a crystal which is built up entirely of coloured ions (fig. 9). In the case in which the foreign ions are

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[6] In contrast to the spectra of most other atoms and ions the spectrum of Mn^{2+} has only been investigated very incompletely. Therefore in fig. 3 Cr^{3+} was chosen instead of the much more commonly occurring Mn^{2+}.

situated at lattice points, and thus replace ions of the basic material, it may even occur that a gradual transition is possible from the case of fig. 10 to that of fig. 9, namely when a regular mixed crystal is formed in which the percentage of the foreign ions is gradually made to increase [7]). As an example of absorption by built-in coloured ions we give in *fig. 11* the absorption spectrum of the mixed crystal Zn_2SiO_4—Mn_2SiO_4 (willemite).

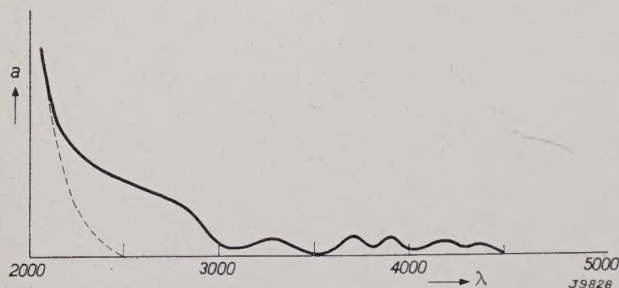Fig. 11. Absorption spectrum of Zn_2SiO_4-Mn_2SiO_4 with 1% Mn.

The absorption is observed at $\lambda < 2500$ Å which is to be ascribed to the transition from SiO_4^{4-} to Zn^{2+}, at $2500 < \lambda < 3000$ Å the corresponding absorption band for the transition from SiO_4^{4-} to Mn^{2+} and finally at $\lambda > 3000$ Å various narrow and weak absorption bands which are to be ascribed to the Mn^{2+} ion itself. Since in all these wavelengthregions the absorption of light leads to fluorescence the absorption spectrum can also be made visible by means of fluorescence. *Fig. 12* shows such a picture.


Fig. 12. Excitation spectrum of willemite (Zn_2SiO_4-Mn_2SiO_4):
a with 1 per mille Mn_2SiO_4, two different exposure times,
b with 1% Mn_2SiO_4.
This spectrum was obtained by projecting the continuous spectrum of a hydrogen tube upon a thin layer of willemite which was separated from the sensitive layer of a photographic plate only by a green gelatine filter which only allows the fluorescence light of the willemite to pass.

The process of fluorescence

As was stated previously, in the case just considered of the crystals which contain foreign ions, fluorescence occurs as a rule, not only when they are irradiated with light of the wave length of the specific absorption bands of the ion (if such are

present), but also when they are irradiated with light whose wave length lies in the region of crystal absorption. What idea must we form in this latter case of the mechanism of fluorescence? In the first place in the region of crystal absorption an electron is brought for instance from an ion B^- to an ion A^+ by the absorption of a light quantum, as is indicated in *fig. 13a* at *1*:

$$A^+ + B^- + h\nu \rightarrow A + B.$$
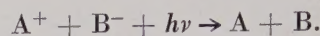
The electron then moves to one of the lower levels of the empty band (*2*), any excess of energy being transmitted to the crystal as thermal agitation, and can travel through the whole crystal. Another method of representation is that the electron in this energy state is passed on from ion to ion:

$$A_1 + A_2^+ + A_3^+ \rightarrow A_1^+ + A_2 + A_3^+ \rightarrow A_1^+ + A_2^+ + A_3 \rightarrow, \text{ etc.}$$
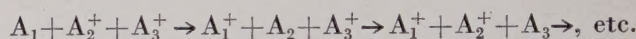
In an exactly similar way the empty place which has been caused by the neutralization of B^- will travel through the crystal, after (*3*) the empty level has moved upwards into the occupied band:

$$B_1 + B_2^- + B_3^- \rightarrow B_1^- + B_2 + B_3^- \rightarrow B_1^- + B_2^- + B_3 \rightarrow \text{ etc.}$$
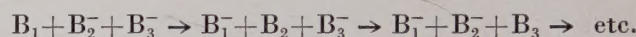
In a completely undisturbed crystal two possibilities would now remain open for the electron:
a) return to the open place in the lower band with the radiation of light of about the same frequency as that of the absorbed light (*4*);
b) return as in a), but without radiation, the energy liberated being converted into vibrations of the crystal lattice (heat vibrations).

Both processes occur. Process b) is the normal conversion of absorbed light into heat. Process a) has been observed in certain crystals (CdS) at a low temperature.
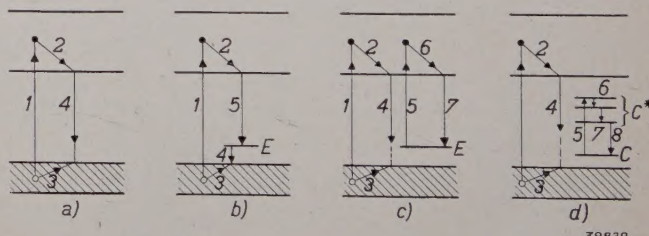

Fig. 13. Possible transitions in a crystal of the ZnS type.
a) without admixture;
b) with "non-coloured" ions built in;
c) idem, sensitized fluorescence;
d) like *c*, but for "coloured" ions.

If the crystal is disturbed by foreign ions (or by a stoichiometric excess of its own ions) and if energy levels lying between the two bands of the crystal (occupied and unoccupied) correspond to these ions, the emission of fluorescence light may take

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[7]) A very good example is the absorption of mixed crystals of lanthanum fluoride (LaF_3) and cerium fluoride (CeF_3), whose spectrum contains characteristic absorption bands which are to be ascribed to the Ce^{3+}-ions and which upon increase of the cerium concentration gradually pass over into the characteristic absorption of pure CeF_3.

place in different ways. In the first place (fig. 13b), after an electron has passed from the full to the empty band (1, 2, 3) the empty place in the lower band may be filled by an electron from the occupied level E (4). The energy which is thereby liberated can return to the now empty level E with radiation (5).

In the second place it is possible that an electron from the empty band returns to the empty place in the occupied band, but in such a way that part of the energy is used to bring an electron from the level E into a higher level, while the excess is given off to the lattice as heat motion.

A similar process is known in the case of free atoms under the name of "sensitized fluorescence". In a mixture of mercury and thallium vapour, mercury atoms can be brought into a state 4.9 eV above the normal state by the absorption of light ($\lambda = 2\,537$ Å). Upon collisions with foreign atoms these mercury atoms can pass into a state at 4.7 V in which the chance of returning to the normal state with light radiation is very slight ("metastable" state). If a metastable mercury atom now encounters a thallium atom, it transmits its energy to the latter, partly in the form of excitation energy and partly in the form of energy of translation (heat). The excited thallium atom then radiates in its own frequency, returning at the same time to the normal state.

In fig. 13c this process is represented for a single level (non-coloured ion), in 13d for a coloured ion.

No matter what process of emission is assumed to take place with the collaboration of foreign ions, it will always be essential for the process of emission that there be a collaboration of an electron (in the empty band) and an empty place (in the full band). It is for this reason that the process of emission in these cases shows similarity, as far as its progress with time is concerned, with a bimolecular chemical reaction. In an earlier communication this was dealt with in more detail. On the other hand the process of fluorescence, which is excited upon radiation in the characteristic absorption bands of coloured ions, exhibits the character of a monomolecular reaction.

The colour of the emission

In the case just discussed of the emission with the collaboration of foreign ions it will be clear that for non coloured ions (level E in fig. 13 b and c) it must be expected that the frequency of the light emitted will depend very much upon the height of the empty band above the occupied level E of the ion. Changes in the position of this band (for instance upon the replacement of the basic material by a similar material of altered composition) have a pronounced effect on the colour of the light emit-

ted. A beautiful example of this is found in the mixed crystals of ZnS and CdS, activated with Cu or Ag. In the case of these crystals, with increasing percentage of Cd the limit of crystal absorption (λ_g) is shifted toward longer wave lengths. As may be seen from the table the maxima of the emission (λ_m) are shifted in the same direction with Cu as well as with Ag as activator.

In the case of the coloured ions, on the basis of the above, no effect on the colour of the emission may be expected by a change in the basic material. The emission proceeds by means of transitions between levels which correspond to more or less undisturbed movements of the electrons within the same ion.

atom per cent ZnS	atom per cent CdS	λ_g Å	λ_m(Ag) Å	λ_m(Cu) Å
100	0	3 360	4 600	5 230
85	15	3 640	4 920	5 790
68	32	3 920	5 410	
50	50	4 270	6 000	
33	67	4 700	6 550	

Colour changes have, however, also been observed here, which probably occur in a different way. In the first place it must be noted that in a substance like willemite the absorption bands of the Mn^{2+} ion lie partly in the ultra violet, while the emitted light is green. This can be interpreted in the following way (fig. 13d): primarily a coloured ion (energy level C) is brought into one of the highest excited states by the absorption of light. From there, via intermediate levels, it passes to the lowest excited level from which the electron returns to the basic state with the emission of radiation.

The transition from one level to the next lower level can be considered to occur directly, the excess energy being given off to the crystal lattice in the form of heat, or via processes of repeated emission and absorption. The latter is possible because of the fact that here also it may be expected that as a result of the collaboration of the crystal lattice the emission line which corresponds to a given absorption transition is shifted slightly with respect to the absorption line toward long wave lengths, and may therefore just coincide with a following absorption line or narrow absorption band. No definite statements can be made about this.

When there is more than one state from which return with emission is finally possible, different competing emission bands occur in the emission, which, when they have a certain width, as is usually the case, may overlap and apparently fuse into one band. If then, due to the influence of the

surroundings on the electron movement in the ion upon change in the basic material, a change occurs in the chances of transition for the two emitting levels, this will cause a change in the distribution of the energy over the two emission bands, with the result of a shift of the maximum and an alteration in the colour. Examples of this mode of behaviour are the following. The dependence of the colour of the emission in the case of ZnS-MnS and (ZnMn)-silicate as a function of the manganese content and of (ZnBeMn)-silicate as a function of the beryllium content.

Phosphorescence

The concept of the energy bands already sketched also furnishes a useful explanation of the phenomenon of phosphorescence. In this case unoccupied disturbed levels (F in *fig. 14*) play a part. It is
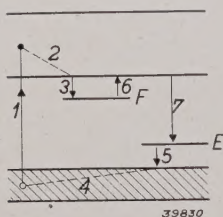

Fig. 14. Mechanism of phosphorescence.

possible that the electron from the empty band reaches these (fig. 14, *3*), while the open place in the empty band is filled by the electron from E (*5*). Return from F to E is then impossible if E and F do not lie very close to each other in space.

Return can then only take place by the electron

first being brought back again from F to the empty band (*6*), which requires energy and is therefore only possible upon addition of energy, for instance from the store of heat of the crystal lattice. Return from F to the empty band can also take place under the influence of irradiation with infra-red or visible light.

When the electron is in the empty band, there is again opportunity of emission (*7*). At sufficiently low temperature and in the absence of external irradiation the state in which the electron is situated in F and in which therefore the crystal possesses a certain excess of energy in reserve may last for a considerable time.

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SOME PARTICULARS OF DIRECTIONAL HEARING

by K. de BOER and A. TH. van URK.   534.76

While the perception of direction in hearing is explained by the time and intensity differences between the sound contributions which the two ears receive, other effects must be sought to explain the localization "in front" and "behind". Several effects which may here play a part are investigated with the help of an arrangement for stereophonic sound reproduction previously described in this periodical.

When listening to a source of sound which does not lie immediately in front of the head of the listener, but at an angle α to the vertical plane bisecting the head (*fig. 1*) the sound does not strike both ears at the same moment and the sound intensity is not the same for both ears. As was discussed in detail in an earlier article in this periodical [1]), the perception of direction which forms a part of hearing is mainly due to these time and intensity differences.
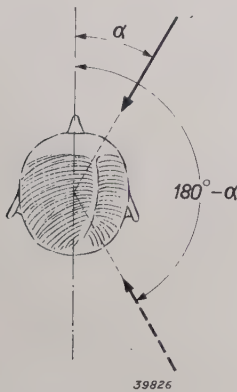

Fig. 1. Sound from a direction which makes an angle α with the direction in which the listener is looking reaches the two ears at different moments and (due to the refraction by the head) with different intensities. If we idealize the head to a sphere, the same time and intensity differences occur with the sound direction $180°-\alpha$ as with the direction α.

By looking fig. 1 in which the shape of the head can be approximated by a sphere, it will be seen that the direction $180°-\alpha$ is equivalent to the direction α as far as the time and intensity differences at the two ears are concerned. From this it would be concluded that the sense of hearing cannot distinguish between two such directions — one in front and one behind the head. Experience shows, however, that the sense of hearing can indeed localize a source of sound as "in front" or "behind". How can this be explained?

The simplest possible explanation starts from the fact that the human head actually deviates from the spherical form. In particular a dissymmetry is caused by the presence of the outer ears or auricles. Since the auricles have a shielding effect for sound waves of very short wave length, *i.e.* for high tones, sounds coming from the back must in general have a duller timbre than sounds from the front. This difference in timbre the hearer is assumed to interpret as a difference between front and back.

We have attempted to test this explanation with the help of an installation for stereophonic sound reproduction previously described in this periodical [2]). Use is here made of a spherical "artificial head" in which two microphones are placed at the ends of a horizontal diameter. Each microphone is connected *via* its own amplifier to one of two telephones over the ears of the listener. Artificial head and listener were now placed in different rooms, while in the vertical plane bisecting the artificial head a source of sound (speaker) was set up (*fig. 2*). Since the artificial head has no auricles, according to the hypothesis given it must be expected that in these tests the listener will be in doubt as to whether the sound comes from the front or the back.
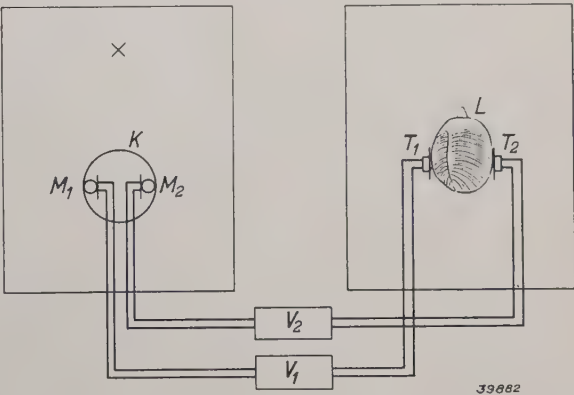

Fig. 2. Arrangement for stereophonic sound reproduction. In the vertical plane bisecting the artificial head K stands a speaker ($\times$). Each of the two microphones M_1, M_2 of the artificial head is connected *via* a separate amplifier V_1, V_2 to one of the two telephones T_1, T_2 at the ears of the observer L who may be in a different room. With this arrangement the observer always hears the sound as if from behind.

[1]) K. de Boer, Stereophonic sound reproduction, Philips techn. Rev. 5, 107, 1940.

[2]) K. de Boer and R. Vermeulen, On improving defective hearing, Philips techn. Rev. 4, 316, 1939. In this article the problem of hearing from "in front" or from "behind" and also several of the experiments here described were already touched upon.

In our experiments this was by no means found to be true. All the persons used for the tests had an absolutely definite perception that the sound came from behind, whether the speaker stood in front of or behind the artificial head.

And still worse: when the sphere of the artificial head was replaced by a well modeled head with ears (large ones at that), the observer still continued unfailingly to hear the sound as coming from behind.

It is possible that this remarkable effect is caused by the fact that we are accustomed to observe a source of sound situated in front of us visually as as well as audibly, and thus upon missing the visual observation we choose the alternative of "behind us". A second possibility is that due to the limited frequency region in which the electro-acoustic apparatus used has a flat characteristic, an undesired auricle effect is introduced: the sound reproduced lacks the highest audible tones and may therefore make an impression of "dullness" on the listener which is interpreted by him as "sound from behind".

Whatever the truth of the matter may be, a decision as to whether the action of the auricles has a share in distinguishing between in front of and behind, cannot be reached in this way. Experiments with an apparatus whose frequency characteristic is flat up to the limit of audibility of about 16 000 c/s would perhaps furnish the desired answer.

In the meantime another explanation of the localization in front or behind also exists, namely that it is obtained by involuntary slight movements of the head of the listener [3]). In *fig. 3* the effect of such a movement is illustrated. If the source stands to the right of the middle, a turn of the head towards the right will bring the sound closer to the middle when it comes obliquely from the front (fig. 3a, b), and the same turn will take the sound farther away when it comes obliquely from behind (fig. 3c, d). The combination of two observations during the turning of the head thus provides an unambiguous conclusion as to the direction of the sound.

This hypothesis can also be very simply tested with the arrangement described. It is exactly the advantage of the arrangement that the different effects which always occur simultaneously and more or less outside the control of the observer in ordinary hearing and whose influence cannot therefore be defined, can now be imitated separately. The effect of slight turns of the head is here investigated by allowing the artificial head and the head of the listener to turn back and forth around their vertical axes synchronously. The synchronism could be obtained in a very simple way by means of a lever in the hands of the speaker near the artificial head by means of which he can turn the artificial head slightly to the right and left in a rhythm which he indicates by counting out aloud. The listener seated in the other room hears the counting in his head phones and turns his head back and forth in the same rhythm. The result now is actually that the perception of "sound from in front" is obtained when the turning of the artificial head and listener's head take place in phase. If they turn in opposite phase, which amounts to the same thing as turning in phase in the case of a diametrically opposite positioning of the speaker with respect to the artificial head, the listener again hears the sound as coming from behind.

It is therefore quite admissible to suppose that in natural directional hearing also the listener ascertains the difference between front and back by small involuntary turns of the head. Such turns of the head occur for example automatically when the observer tries to see the source of sound, but also without this the head always makes slight, more or less reflex motions which may already furnish the desired effect.
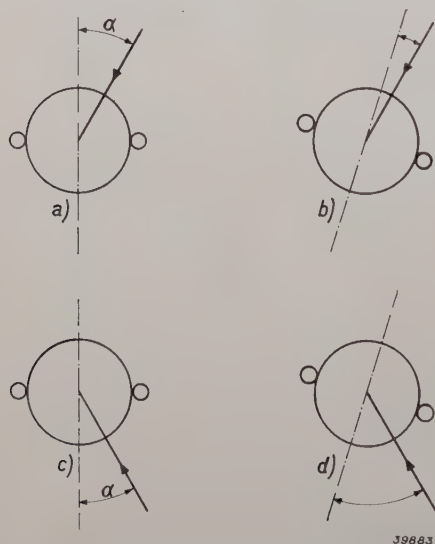

Fig. 3. While the two sound directions indicated in (a) and (c) cannot be distinguished by the observer, the difference is easily ascertained after a slight turn of the head (b and d).

[3]) J. L. van Soest, Physica **9**, 271, 1929; H. Wallach, J. Acoust. Soc. Amer. **10**, 270, 1939.

In the experiments last described it is very tempting to try to confuse the hearing, namely by not moving the artificial head and the listener's head in the same way. The motion in "opposite phase" was already a sample of this, to which, however the hearing promptly furnished the correct answer. What will happen if we allow the artificial head

and the listener's head to turn with different amplitudes? If we make the amplitude of the listener's head very small or equal to zero, while the artificial head turns with a large amplitude, a new phenomenon occurs: the listener simply hears the sound move back and forth according to the relative motion of the speaker with respect to the artificial head. If conversely we allow the head of the listener to turn back and forth while the artificial head moves less or not at all, a new impression is received: there is a perception of a definite direction of sound which no longer lies in the horizontal plane but possesses a certain angle of elevation.

This effect fits perfectly into the frame of the theory presented when it is kept in mind that a certain time and intensity difference of the sound at the two ears can actually be realized not only by one direction in front of (angle a) and one direction behind (angle $180°-a$) as was sketched in the diagram on a plane in fig. 1, but by all directions which lie on a cone with the semi apex angle $90°-a$ around the axis of the ear, see *fig. 4*.

The choice among all these directions can be brought about in natural hearing with the help of the above mentioned slight turns of the head.
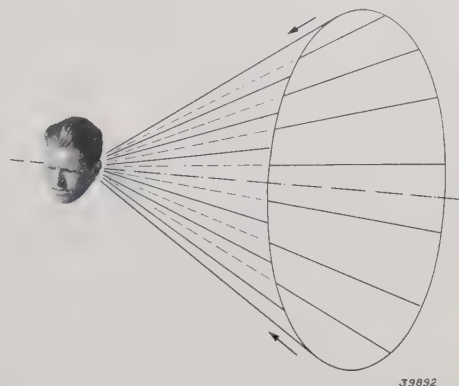

Fig. 4. Time and intensity differences are not equally great only for one direction forward and one direction backward, but for all directions which constitute the lines describing a cone about the axis of the ears of the observer.

To each position of the head corresponds a definite cone of directions, and the true direction of the source of sound must therefore be the common
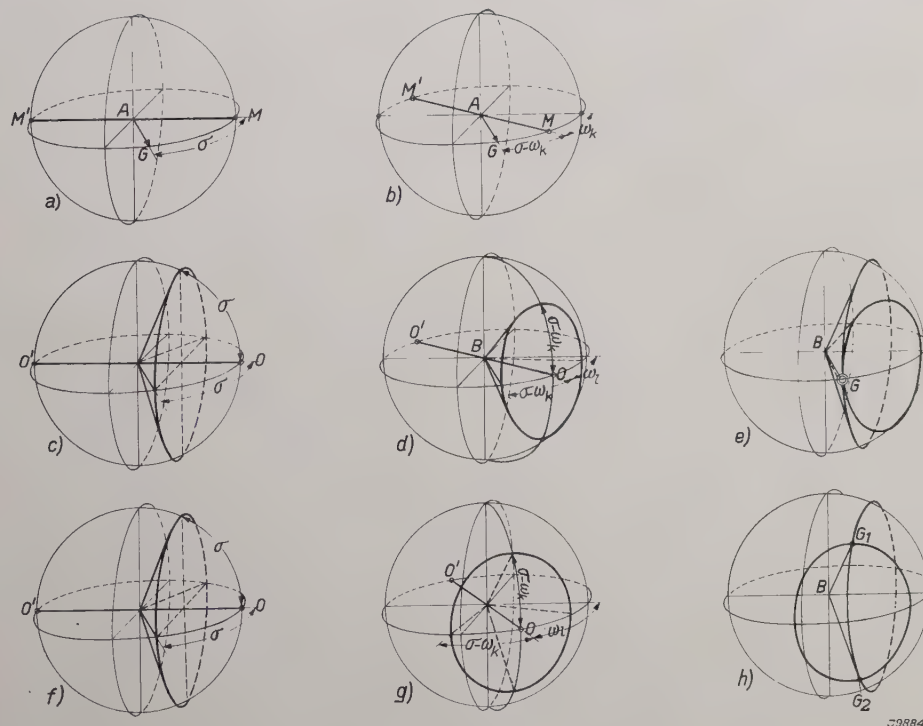

Fig. 5a en b). Axis of the ears MM' of the artificial head and direction AG of the source of sound before and after turning the artificial head through an angle ω_k.
c and d) Axis of the ears OO' of the listener and cone of the possible sound directions before and after the simultaneous turning of artificial head (angle ω_k) and listener's head (angle ω_l). In this case ω_l is assumed to be equal to ω_k. e). The two cones touch each other along the line BG.
f and g) The same as in c and d, but for the case where $\omega_l > \omega_k$. h) The two cones intersect each other in two lines BG_1 and BG_2, which deviate upwards and downwards, respectively, from the horizontal plane.

line of intersection of two or more such cones [4]).

This now also occurs in the experiments with the artificial head. The source of sound stands in the horizontal plane through the axis of the ears of the artificial head, in a direction which makes an angle σ with the axis of the ears (*fig. 5a*). The listener must choose the direction of the sound on a cone with the semi apex angle σ, see fig. 5c or f. If the artificial head now turns through an angle ω_k (fig. 5b) the angle between axis of ears and direction of sound becomes $\sigma-\omega_k$, the new cone of directions for the listener thus also takes on the semi apex angle $\sigma-\omega_k$; the axis of this cone has turned with the head of the listener through an angle ω_l. If $\omega_l = \omega_k$ (fig. 5d) as in the experiments initially described, the old and the new cone t o u c h each other at a line in the horizontal plane which makes an angle σ with the old direction of the axis of the ears (fig. 5e). No angle of elevation is here observed and the sense of hearing takes a decision as to front or back only by means of the turn. If, however, $\omega_l > \omega_k$, see fig. 5g, then the old and the new cones clearly i n t e r s e c t each other in two lines which make a certain angle ϑ upward or downward with the horizontal plane (fig. 5h) [5]).

The angle of elevation which must be observed in carrying out the experiment with certain angles ω_k and ω_l can easily be calculated according to the rules of spherical trigonometry. In *fig. 6*
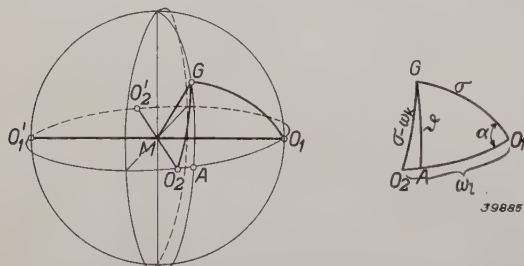

Fig. 6. The angle of elevation ϑ of the sound direction, which is observed according to fig. 5h upon turning the listener's head back and forth with greater amplitude than the movements of the artificial head, can be calculated with the help of the spherical triangles O_1AG and O_1O_2G.

O_1O_1' is the first position of the axis of the ears of the listener, O_2O_2' the second position, while MG represents the line of intersection of the two cones of observations (we consider only the one directed

upwards). In the spherical triangle O_2O_1G the side $GO_1 = \sigma$, since G lies on the cone with semi apex angle σ and axis O_1O_1'. Further the side $GO_2 = \sigma-\omega_k$, since G also lies on the cone with semi apex angle $\sigma-\omega_k$ and axis O_2O_2'. Finally the side $O_2O_1 = \omega_l$, namely the angle through which the head of the listener was turned. For the angle α in the spherical triangle mentioned we now find

$$\cos \alpha = \frac{\cos (\sigma-\omega_k) - \cos \sigma \, \cos \omega_l}{\sin \sigma \, \sin \omega_l};$$

while the required angle of elevation ϑ of the direction MG can be calculated from the right-angled spherical triangle O_1AG, namely

$$\sin \vartheta = \sin \alpha \cdot \sin \sigma.$$

If one considers only the case in which the source of sound in the state of rest lies in the v e r t i c a l p l a n e bisecting the artificial head, so that $\sigma = 90°$, the formulae become simpler and one finds directly the relation between ω_k, ω_l and ϑ:

$$\cos \vartheta = \frac{\sin \omega_k}{\sin \omega_l} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

For the extreme case where $\omega_k = 0$ (artificial head stationary, only the listener's head turns back and forth) this whole method of representation is easily verified. The listener must always hear a source of sound which stands in the vertical plane bisecting the artificial head directly a b o v e or b e l o w himself, since $\cos \vartheta = 0$, $\vartheta = 90°$. This is indeed immediately clear, because the artificial head, and thus also the listener always hears the same thing in this experiment, and this is only possible when the listener's head turns back and forth around a vertical axis, at a position of the source of sound at the zenith or nadir. This observation was indeed confirmed in the experiments, with the expected uncertainty between "above" and "below" some observers always heard the sound from above, others from below, from their own abdomen.

For angles $\omega_k \neq 0$ equation (1) is not so easy to verify, since in order to do so the head of the listener and the artificial head must move synchronously each with an accurately determined amplitude. This could be realized with the arrangement represented in *fig. 7*. Artificial head and observer are in two adjacent rooms which are separated by a sound-proof glass wall. A pointer with a white disc is attached to the artificial head and this is watched by the observer. When (without turning his eyes) the observer follows the white disc as the artificial head turns, his own head turns synchro-

[4]) The "construction" in this way of an angle of elevation is usually quite difficult for the ear, it therefore prefers to use a kind of zero-point method: with a sound coming obliquely from above the head is involuntarily put into such an oblique position by trial and error that the direction of the sound is brought into the "horizontal" plane through the axis of the ears.
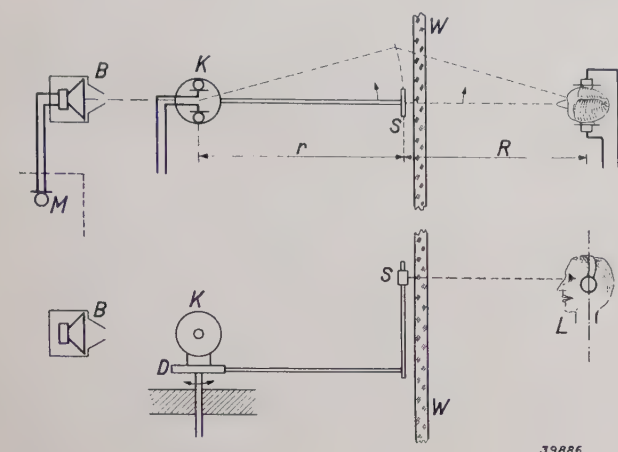
[5]) The decision between "above" and "below" can be obtained in natural hearing by turning the head about a different axis.

nously with the artificial head and there is a definite relation between the two amplitudes. This relation can be varied very simply by changing

Fig. 7. Arrangement for the experimental determination of the observed angle of elevation when the angles ω_k and ω_l are different. K artificial head, L listener's head, W soundproof glass wall. B source of sound (loud speaker with very small opening connected with a microphone M set up in another room, before which stands a speaker), D turntable on which the artificial head is mounted and to which is fastened a lath with a white disc S as pointer.

the length of the pointer (r) or the distance between observer and glass wall (R). In order to fix satisfactorily the relative position between source of sound and artificial head, a loud speaker with a very small opening is placed in front of the artificial head. The fact that the artificial head and the listener's head here turn in opposite directions can of course be corrected by a suitable connection of the two head phones of the observer. The white disc is adjustable in height in order to be sure that the head of every observer actually turns about a vertical axis.

With this arrangement the perception of every angle of elevation between 0 and 90° could be obtained. A certain difficulty occurred, however, in measuring the angles of elevation observed. The observer could of course indicate with outstretched arm the direction perceived, but this was not found to be a suitable method for measuring the angle. Therefore use was also made of the fact that together with the perception of direction there is also a certain perception of distance which depends upon the intensity of the sound. With a certain intensity of the sound the observer has the feeling that the source of sound is situated on the outside of his head, whereupon he can indicate the spot (the sound image) with his finger [6]). In this way the angles of elevation observed (angle between the horizontal plane and the perpendicular from the

sound image to the axis of the ears) could be measured with sufficient accuracy.

In *fig. 8* we have plotted the calculated and measured angles of elevation ϑ as functions of each other [7]). Theoretically all the points should lie on the 45° line. The agreement is as good as could be expected in these difficult measurements.

If we consider the experiments described as attempts to confuse the ear, it is clear that the sense of hearing possesses sufficient adaptability to find an unambiguous solution in all kinds of peculiar situations. It sometimes even registers perceptions which it certainly could not have learned from experience, but which are as it were extrapolated. Thus the localization of sounds inside the body — especially in the head, see footnote [4]) — or the perception of direction previously discussed (see the article cited in footnote [1])), which is caused by differences in time which are many times greater
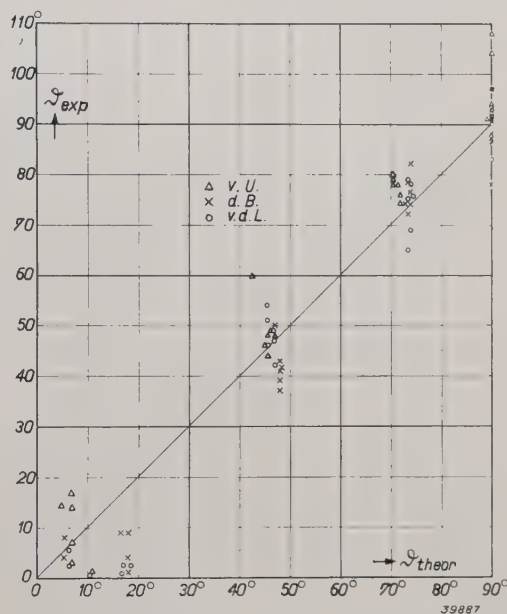

Fig. 8. The elevation angles ϑ_{exp}. with different turns of artificial head and listener's head plotted against the angles calculated ϑ_{theor}.. The triangles, circles and crosses refer to three different observers. The points measured show great scattering but no systematic deviation from the theoretical 45° line.

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[6]) It is then remarkable that one observer hears a more intense source of sound farther away, while another still "closer", *i.e.* in the head! For a weaker source of sound the reverse is then true.

[7]) In the calculation of ϑ a correction must still be introduced because of the fact that the heads of the observers compared with each other and with the artificial head do not have the same diameter. In our case the artificial head had a circumference a_k, which was smaller than the circumference (a_l) of all the observers' heads. Upon a turn ω_k of the artificial head therefore the time and intensity differences at the microphones are too small. This was taken into account roughly by inserting in equation (1) instead of the true angle ω_k, a smaller angle $\omega_k \cdot a_k/a_l$.

than the maximum differences in time of arrival at the two ears which can occur in normal hearing.

Nevertheless the sharpness of hearing also has its limits, and these are apparently exceeded when in the experiments for the measurement of the angles of elevation observed we exchange the two head phones of the listener. With e q u a l turns back and forth of artificial head and listener's head, $\omega_k = \omega_l$, as was to be expected, the perception occurs that the sound comes from b e h i n d. With unequal turns, on the other hand, with $\omega_l > \omega_k$, whereupon the ear should register an a n g l e of e l e v a t i o n t o w a r d s t h e r e a r, the perception becomes very vague and difficult to define. In *fig. 9* a comparison is given between the elevations observed and those calculated for this case. The spreading is greater than in fig. 8, the measured points with $\vartheta_{\text{theor.}} \approx 65°$ all lie too low, some measurements here are entirely wrong. It is remarkable that in these measurements much more clearly than in the measurements in front, the theoretically expected indefiniteness occurred between directions a b o v e and b e l o w the horizontal plane. Of the three observers whose measurements are reproduced in fig. 9 one always heard the sound above, one always below and one could

localize it at will either above or below the horizontal plane, while in the measurements of fig. 8 the localization was quite regularly a b o v e the horizontal plane.
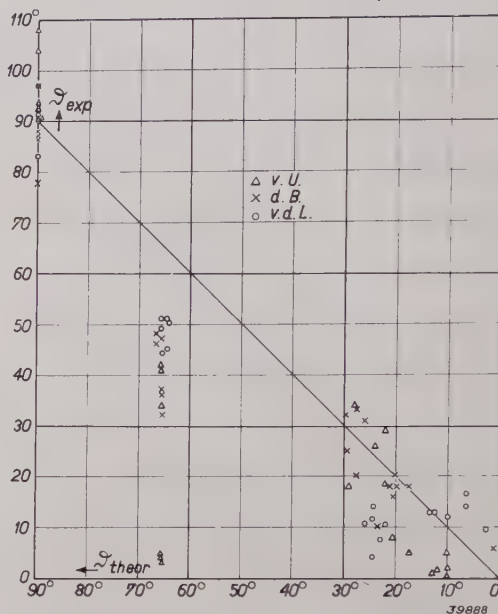

Fig. 9. As in fig. 8, but for sound directions f r o m b e h i n d. The measured points for $\vartheta_{\text{theor.}} = 90°$ (artificial head stationary) are of course the same as in fig. 8.

THE PERMEABILITY OF METAL WALLS FOR GASES

by J. D. FAST.

620.193.29

A survey is given in this article of the phenomena which play a part in the permeation of gases through metal walls. It is pointed out that the gases in the metal are present in atomic (or perhaps ionic) form, and that they move in the space between the atoms of the crystal lattice without this movement being necessarily accompanied by a diffusion of the metal itself. Attention is also called to the part played by the processes which take place at the surface of the metal, namely the dissociation into atoms and the recombination to molecules, respectively, and the penetration into and the emergence from the metal, respectively, of the atoms.

Introduction

In different types of high vacuum tubes the walls are made wholly or partly of metal. In some cases this type of construction is employed in order to obtain effective cooling by means of running water, in other cases in order to ensure a simplified method of mass production.

The problem of mass production is particularly important in the case of radio valves where in different cases the glass walls have been replaced by metal.

The cooling problem is of particular importance in transmitter valves, rectifier valves, X-ray tubes and the like, in which in every case only a part of the energy supplied can be converted into the desired form and where the dissipation of the lost heat energy in high-power tubes forms one of the most important problems.

Although in such cases metal walls offer advantages over glass walls, difficulties may also occur in their use which are almost entirely absent when glass is used. One of the most important of these is the fact that upon contact of the outside surface with cooling water as well as with gases the vacuum on the inside may under certain circumstances deteriorate, due to the fact that gases diffuse to the inside through the walls. In this article we shall try to explain the ideas which may be gained of this transmission of gases through metal walls. It will be found that the phenomenon is more complicated than is expressed by the term diffusion. In addition to this latter process, which takes place inside the metal, we are also concerned with processes which take place on the surfaces of entrance and emergence. From the discussion the relation will also appear which exists between the transmission and other more familiar phenomena which occur upon contact between gases and metals, such as adsorption and solution.

The mechanism of diffusion in metals

Geometric and chemical factors

At first glance it will seem strange that gases should be able to move through compact metals, and the first question which arises is about the mechanism of this process. It should be stated in advance that very little is yet known with certainty about it. In the attempt to form an idea of the different possibilities we shall not therefore limit ourselves to the diffusion of gases, but shall treat the phenomenon of the transport of matter in solid metals more in general.
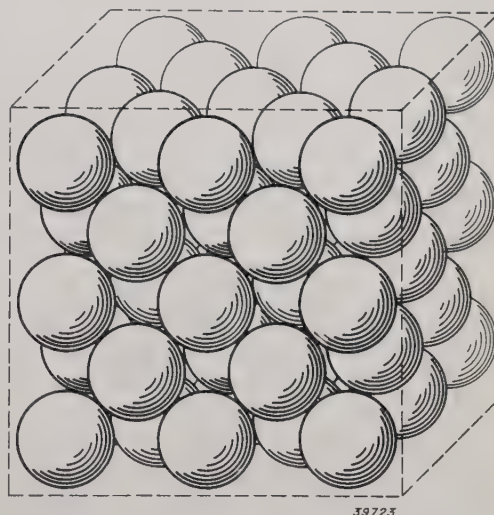

Fig. 1. Closest cubic packing. The lattice is face-centred. Examples of metals which crystallize in this way are: copper, silver, aluminium, nickel, palladium, platinum and furthermore carbon-free iron above 900 °C.

A primitive idea can be obtained of the structure of a metal crystal by considerng it to be built up of atoms in the form of small hard spheres with a radius of about 10^{-8} cm, which are packed together in such a way that a regular three-dimensional lattice results. In the case of most metals the symmetry of the lattice is such that the spheres fill the available space as closely as possible. This can be attained by two different ways of packing and leads to the familiar structures with cubic and hexagonal closest packing. In both cases 74 per cent of the total volume is occupied by the spheres. In

figs. 1 and 2 the arrangement of the atoms for these two closest packings are represented. Another group of metals has a slightly less close packing
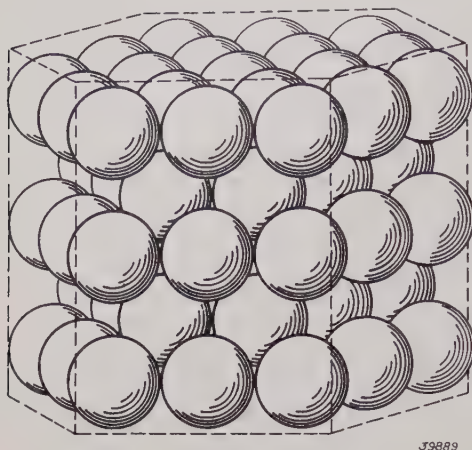

Fig. 2. Closest hexagonal packing. Examples of metals which crystallize in this way are: beryllium, magnesium, titanium and zirconium, the last two below their respective transition points at 885 and 865 °C.

with cubic body-centred structure, in which the spheres occupy 68 per cent of the available volume (see *fig.* 3).

With the picture of a metal crystal just given it is difficult to imagine the occurrence of diffusion, unless it be that of foreign atoms (likewise considered to be spherical) which are very small compared with the metal atoms. Foreign atoms can only move unhindered through the sphere arrangements described when they are even smaller than the largest spheres which could be placed in the cavities between the large packed spheres.

The image of a metal crystal as a symmetrical arrangement of hard spheres is of course much too primitive. The idea which is now held of the struc-

ture of a metal is that of a three-dimensional lattice of positive ions which (floating freely as it were) are situated in a dense electron "gas", which gas uniformly fills the spaces between the ions. Due to mutual electrostatic repulsion the ions tend to remain as far away from each other as possible. The mutual distances are here determined in such a way that the pressure of the electron gas and the electrostatic attraction between ions and electrons maintain an equilibrium which at the same time results in the arrangement in a regular lattice. The image of the symmetrically arranged spheres can now if desired be transferred to the ions, but the spheres must now no longer be considered as entirely hard, while moreover they need not touch each other [1]. In the case of the alkali metals the ions lie at relatively great distances apart, in the case of many other metals they lie closer together. In *fig.* 4 the position of the ions in the electron gas for the closest packed lattice planes is shown for the metals sodium and copper [2]. In sodium about 70 per cent of the volume of the metal is occupied by the electron gas. In copper, a subordinate series metal, on the other hand, the ions are so close to each other that a certain mutual penetration of their electron shells even occurs.
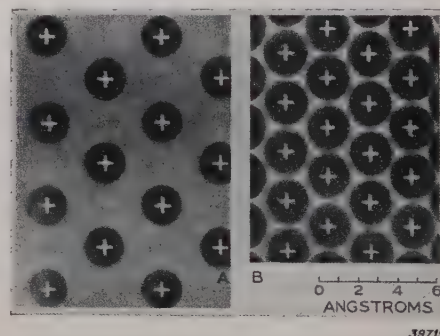
Fig. 4. Arrangement and true relative size of the ions in the most densely occupied lattice planes of sodium and copper according to Shockley. The boundaries of the ions are idealized, actually the density of electrons decreases gradually from a high value inside the ion to a much smaller constant value outside of it.

The spaces between the atoms may therefore in many cases be larger than would be expected on the basis of the primitive picture. On the other hand, these spaces are not empty, as in the primitive con-
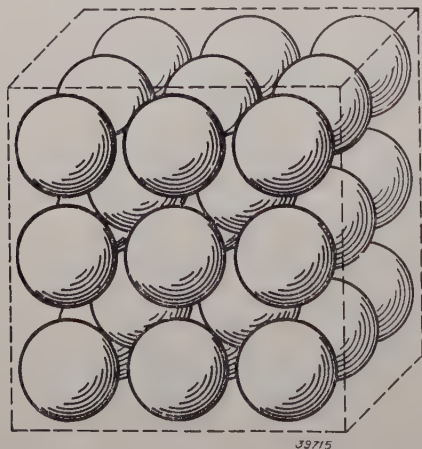

Fig. 3. Cube centred lattice. This packing is less dense than that in figs. 1 and 2. Examples of metals which crystallize in this way are: the alkali metals, tantalum, tungsten and iron below 900 °C.

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[1] If the modern idea of an atom (or ion) as a positive nucleus surrounded by a cloud of electrons is kept in mind, the concept of "touching" already becomes very vague.

[2] The figure is borrowed from an article by W. Shockley, J. Appl. Phys. **10**, 543, 1939. References to the literature are here made only when no reference was made to it in a publication which will shortly appear in "Physica" under the same title. For further literature references therefore the reader should consult that article.

cept, but filled with electrons. A diffusion of a gas through a metal is therefore scarcely conceivable without considerable reciprocal action between the two substances. It may therefore be expected that the diffusion of gases through metals will in general be of a specific character. It is found indeed that a gas is only able to dissolve in a metal and diffuse through it when there is a certain "chemical affinity" between the two. Thus for instance oxygen can be taken up by copper and silver and can also diffuse in these metals, nitrogen on the other hand cannot do this, while chemically also it has little tendency to combine with these metals. The latter gas can, however, at sufficiently high temperatures, diffuse through iron and alloys of iron and chromium, while compounds of these metals with nitrogen are known. The rare gases, which form no chemical compounds, are insoluble in all metals and diffuse through none of them.

Influence of temperature

In order to understand the occurrence of diffusion in a solid metal wall, it must also be kept in mind that not only do the foreign atoms execute a heat motion, which makes the diffusion possible, but that the lattice ions also do so in the form of vibrational movements around their positions of equilibrium. With increasing temperature this causes at the same time an expansion of the whole lattice. The presence of the gas itself causes in addition an extra deformation (expansion) of the lattice. All these factors create in many cases a possibility, even for relatively large atoms, of moving by jumps through the metal lattice from interstice to interstice at temperatures which are not too low. In doing this they must as it were push through between the ions of the lattice at suitable moments, thereby overcoming repulsive forces. Thus only those atoms can make a "jump" which possess at least a definite energy E, which will usually be large compared with the average energy of the atoms. That such atoms which are rich in energy are also present at thermal equilibrium is due to the fact that according to the Maxwell-Boltzmann law of distribution the energies extend to very high values. The fraction of the atoms which have at least a certain high energy E is given by:

$$\frac{\Delta N}{N} = e^{-E/kT} = e^{-Q/RT} . \quad . \quad . \quad (1)$$

(E = energy per atom, k = Boltzmann's constant, Q = energy per gram atom, R = the gas constant). From this it follows that the degree to

which the "jumps" occur is determined in the first place by the temperature, and that the diffusion constant δ will be approximately proportional to the factor given by equation (1) in which the name heat of diffusion can be given to the "activation energy" Q.

We thus find that

$$\delta = Ae^{-Q/RT}, \quad . \quad . \quad . \quad . \quad (2)$$

where A is a constant.

Solution and diffusion by substitution

The form described of diffusion of atoms of an element B through the interstices of the lattice of an element A will be expected especially when the atomic volume of B is relatively small and the atoms of B can be easily deformed (for instance elements with a low atomic number such as hydrogen, boron, carbon, nitrogen and oxygen), or when the lattice of A has especially large interstices. This expectation is naturally coupled with the assumption that the substance A permits the presence of atoms of B in its lattice interstices, that is to say that A possesses a certain solvent capacity for B. This, as was mentioned in the preceding, is determined not only by geometric but also by chemical factors [3].

In addition to the form of solution and diffusion considered until now, however, the case often occurs in which the foreign atoms B occupy positions in the lattice which in the pure metal A are occupied by atoms of A. This is the case, in particular, upon the solution of a foreign metal in another metal. Diffusion phenomena may also occur in such substitutional solid solutions under suitable conditions, whereby any possible differences in concentration are equalized. Different conceptions may be formed of the mechanism of diffusion in substitutional solid solutions. It may for example be assumed that at a sufficiently high temperature a foreign ion B changes place here and there in the lattice with an adjacent ion A, so that two ions are concerned in each "jump". It is, however, more probable that only one ion is concerned in each "jump". It must then be assumed that at high temperatures in substitutional solid solutions also a small part of the atoms are present in the interstices of the lattice, or that there are unoccu-

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[3] Strictly speaking it is not permissible to make a sharp distinction between chemical and geometric factors, since all the forces active in the binding, even the repulsive forces, with which any spatial limitations occurring are closely connected, must be considered as belonging to the "chemical" forces.

pied positions in the lattice. In the first case the diffusion occurs in the way already discussed, namely by "jumps" from interstice to interstice. In the second case an ion can jump to an adjacent unoccupied position, and it is clear that a diffusion current of ions in a given direction according to this mechanism is equivalent to a current of unoccupied positions in the opposite direction. In considering fig. 4 both types of "defects", namely unoccupied positions and ions in the interstices can be imagined in a metal like sodium. In a metal like copper on the other hand one can in the first instance imagine the presence of unoccupied places only.

In the so-called theory of disturbed order of Wagner and Schottky [4]) it is assumed that at a temperature above the absolute zero point a crystal, in the thermodynamical equilibrium state always contains a number of the "defects" spoken of. If these reversible defects of atomic dimensions are held responsible for the diffusion, the foreign atoms B and the lattice atoms A move independently of each other in the first instance. However, the movements are correlated with each other in as much as the current of foreign atoms B in the one direction cannot be larger than the maximum possible current of atoms A in the other direction. If it were otherwise the character of substitutional solid solution would be lost. The velocity of transport of B is limited therefore by the velocity of self-diffusion of A, which is in general small.

Hydrogen-iron and oxygen-zirconium

Making use of the conclusion just deduced, it can immediately be shown for different solutions of gases in metals that one is certainly not concerned with substitutional solid solutions. Thus for example hydrogen in metals like palladium and iron already exhibits high diffusion velocities at temperatures below 100 °C, although there is certainly no question of an appreciable self-diffusion of the pure metals or of the metals containing hydrogen. It might now be assumed that in this case the movement of the hydrogen takes place along the crystal boundaries. The metals employed technically never consist of a single crystal, but of many crystals grown together. These crystals exhibit great relative differences in orientation, and it is clear that the packing of the atoms (ions) at the boundaries will be less perfect than in the interior of the crystals. Cases are indeed

known in which the diffusion takes place primarily along these boundaries. A familiar example is the diffusion of thorium through tungsten [5]). For the system iron-hydrogen, however, it could be shown that the permeability of a single crystal is the same as that of a polycristal, so that the movement undoubtedly here takes place through the lattice.

In other cases there is a possibility of demonstrating the occurrence of the interstitial type of solution from a combination of X-ray measurements of the lattice constants and direct measurements of the specific weight. Thus for example the specific weight of zirconium is found to increase upon the absorption of oxygen, although oxygen atoms are much lighter than zirconium atoms. This already indicates an occupation of the interstices and not a substitution. unless a contraction of the lattice due to the presence of oxygen is assumed. In an X-ray examination, however, the distances between the zirconium atoms were found to have become greater. There is even a quantitative agreement between the directly measured (with a hydrostatic balance) specific weight and the value calculated from the lattice constants and the composition, if in the calculation it is assumed that all the oxygen is taken up in the interstices and no zirconium atoms in the lattice are replaced by oxygen.

Until now no cases are known in which gases form substitutional solid solutions with metals. In agreement with these gases, as far as they are soluble, exhibit in general high diffusion velocities in metals.

State of charge of the dissolved gas

From the occurrence of the interstitial type of solution and diffusion, for geometrical reasons it may be prophesied with fairly great certainty, as was tacitly assumed above, that the gases will be present in the metal, not in the form of biatomic molecules (H_2, O_2, N_2, etc.) but split into atoms. In agreement with this it is found in solubility experiments that the concentrations in metals of the gases mentioned increase at constant temperature with the square root of the pressure of the gas outside the metal.

By making use of modern conceptions about the metallic state we arrived in the foregoing at a picture of diffusion in pure metals and alloys in which it were not neutral atoms but ions which diffuse. It will further be expected that gases also in the medium of metal ions and electrons will not be present in the form of neutral atoms, but will in general

[4]) C. Wagner and W. Schottky, Z. phys. Chem. B **11**, 163, 1930.

[5]) P. Clausing, Physica **7**, 193, 1927.

carry an electric charge. It is found indeed in the few cases in which this phenomenon has been sought that electrolysis effects can occur in solutions of gases in solid metals. Under suitable conditions of temperature and field strength hydrogen in palladium moves toward the cathode, while nitrogen in iron and oxygen in zirconium move toward the anode. Because of the fact that these gases are present in the interstices of the lattice and have a relatively high mobility there, it may be concluded with a fair degree of certainty that hydrogen has a positive charge and nitrogen and oxygen negative charges. This does not mean that clearly distinguishable H^+ and O^{--} ions must be assumed, but rather that the distribution of the electron gas is such that considering an average over a longer time the hydrogen atoms carry a deficit and the oxygen atoms an excess of negative charge.

If we were concerned with substitutional solid solutions the conclusion about the sign of the charge would certainly not have been permissible. Let us for example assume that the motion in this case takes place *via* that type of reversible "defects" in which a very small fraction of the atoms are situated in the interstices. A and B then move independently of each other in the first instance and the concentration at the cathode will increase for that component for which the product of concentration C in the interstices, charge z and diffusion constant D has the largest positive value [6]. The magnitude of the ionic current is determined not only by the number of mobile charge carriers, but also by their velocity, and in an electric field of a given intensity the latter is proportional to the product zD.

If on the other hand it were assumed that in the substitutional solid solutions mentioned the motion takes place by direct exchange of place of approximately equally large A and B ions, it would be expected that the concentration of the ions with the largest positive charge will increase at the cathode, since the potential energy thereby decreases. If A and B do not have about the same atomic volume, so that a change in the lattice constant occurs due to the changes in concentration, then for the same reason it will be expected that the direction of motion will be determined not by the charge, but by the density of charge, *i.e.* by the quotient z/v (v = atomic volume). Schwarz[7] has shown that this is the case with liquid alloys (amalgams).

If the hydrogen is actually present in the metals more or less as positive ion, unusually high diffusion rates may be expected for this gas. A positive hydrogen ion is nothing else but a hydrogen nucleus, a proton, whose dimensions are negligibly small compared with those of an atom (the radius of an atom is of the order of magnitude of 10^{-8} cm, that of a proton about 10^{-13} cm). Even at room

temperature indeed hydrogen is found to be able to move through different metals, The velocities are, however, smaller than would be expected in case of a complete dissociation into protons and electrons. If, conversely, at a relatively low temperature an unknown gas permeates through a metal wall, the first thought will be that it is hydrogen.

For the sake of completeness we wish to point out that it is not impossible that the dissolved hydrogen ions bear a negative charge in certain metals, particularly the alkali and alkaline earth metals. We shall consider sodium as an example. An investigation by Hüttig and Brodkorb [8] has shown that it is probable that this metal can contain 3 to 5 atomic per cent of hydrogen in solid solution, and that only after this amount has been exceeded is the hydride NaH formed. In this compound the hydrogen more or less plays the part of a halogen, and it seems obvious to assume that the dissolved hydrogen atoms also carry a negative charge and in electrolysis experiments will move toward the anode, but with much lower velocity than that with which in iron or palladium for instance they move toward the cathode.

The part played by the boundary surfaces when gases pass through metal walls

In the preceding we have spoken only of the movement of gases in the interior of solid metals. Since the gases diffuse in the form of atoms (or ions) it is obvious to assume that they can only penetrate a metal wall after a splitting of the molecules into atoms (or ions) has taken place on the entrance surface. On the emergence surface the reverse process (the recombination to molecules) must take place before the gas can leave the metal. In order to make the description of the permeation of gases through metal walls complete, therefore, in addition to the diffusion in the metal we must also consider the phenomena which take place in the adsorbed layer.

Two different types of adsorption of gases on metals can be distinguished. At a low temperature (for instance at the temperature of liquid air) so-called physical adsorption takes place, in which the gas is bound in a molecular form by van der Waals forces, *i.e.* by forces which are of the same nature as the forces of attraction acting between the molecules of gases, which are responsible for the deviations from the equation of state of the ideal gas and for condensation at low temperatures. This

[6] C. Wagner, Z. phys. Chem. B **15**, 347, 1932; Z. phys. Chem. A **164**, 231, 1933.

[7] K. E. Schwarz, Elektrolytische Wanderung in flüssigen und festen Metallen, J. A. Barth, Leipzig 1940.

[8] G. F. Hüttig and F. Brodkorb, Z. anorg. Chem. **161**, 353, 1927.

adsorption decreases with increasing temperature. At higher temperatures so-called activated adsorption takes place in which chiefly chemical forces are active [9]. This type of adsorption is distinguished from the van der Waals adsorption by a much higher heat of adsorption, the existence of an activation energy and a more specific character. It is accompanied by dissociation of the gas into atoms and thus forms the required link in the process of permeation.

The fact that activated adsorption is actually accompanied by a splitting into atoms (thus for instance in the case of H_2 by the formation of a surface hydride) is illustrated in perhaps the most convincing way by experiments on the simultaneous adsorption on metals in powder form of ordinary hydrogen H_2 and the isotope of hydrogen D_2 with double the atomic weight (deuterium). In the temperature region of van der Waals adsorption the molecules of H_2 and D_2 are freed as such upon desorption. In the temperature region in which activated adsorption occurs a partial conversion into HD must be expected. If we assume for example that an H_2 and a D_2 molecule are adsorbed side by side on the metal surface according to the schematic representation below (fig. 5) it will be seen that upon desorption there is approximately just as great a chance that the gas will be freed in the form of $H_2 + D_2$ as in the form of 2 HD [10]. The results of experiments are in agreement with this conception [11].
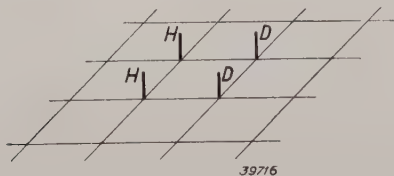
Fig. 5. Atomic adsorption of $H_2 = H + H$ and $D_2 = D + D$ on a metal surface. Possibility of the formation of HD by recombination.

The phenomena occurring upon adsorption and desorption are represented very comprehensively by a scheme of potential curves [12]. Curve 1 of

fig. 6 relates to the adsorption of a hydrogen molecule; curve 2 to that of two hydrogen atoms. The splitting of the molecule into atoms at a large distance from the surface requires the dissociation
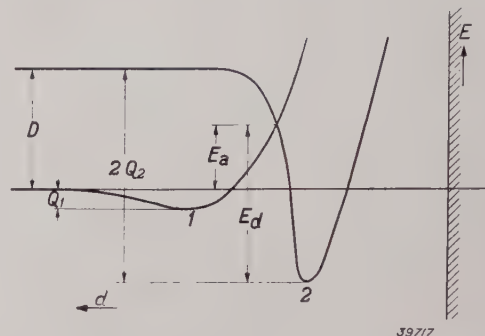
Fig. 6. Potential curves for van der Waals adsorption (1) and atomic adsorption (2) of hydrogen. Q_1 = molecular adsorption energy, Q_2 = atomic adsorption energy ($2Q_2$ idem for the adsorption of two atoms). E_a is the activation energy of the atomic adsorption; E_d idem for desorption (recombination), D is the dissociation energy of the free molecule.

energy D. Q_1 is the heat liberated in physical adsorption, $2Q_2-D$ that liberated in activated adsorption (Q_2 is here the adsorption energy of one hydrogen atom, taken strictly at the absolute zero point and neglecting the zero point vibration). The height E_a of the intersection of the two curves above the zero line gives approximately the activation energy of activated adsorption. E_d indicates approximately the activation energy of desorption.

In the cases in which the gas atoms in the dissolved state carry an electric charge a binding in the form of neutral atoms will not be expected in activated adsorption. In the case of hydrogen for example, in the activated adsorption of each H-atom the electron will already be more or less taken up by the metal. In agreement with this it is found that the adsorption of hydrogen by many metals causes a lowering of the work function of the electrons. Conversely, the adsorption of oxygen causes an increase in the work function [13].

Upon the passage of a gas through a metal wall, after the formation of atoms (or ions) on the surface, a new activation energy must be supplied to bring the atoms from this (chemisorbed) state into the interior of the metal. In the metal itself, for every jump from interstice to interstice, the activation energy of diffusion must be supplied. Upon reaching the surface of emergence an activation energy must again be supplied to cause the atoms to pass from the dissolved to the adsorbed state. As

[9] H. S. Taylor, J. Amer. Chem. Soc. 53, 578, 1931.

[10] In the temperature region concerned with permeability one must not, as is suggested by the figure, expect a binding of the H and D-atoms at fixed positions, but a state in which a large fraction is always moving from point to point over the surface by means of "jump"-like movements. This, however, makes no difference as far as the result to be expected is concerned.

[11] M. Polanyi, Sci. J. Roy. Coll. Sci. 7, 21, 1937; A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge University Press, Cambridge 1935.

[12] J. E. Lennard Jones, Trans. Faraday Soc., 28, 341, 1932.

[13] Cf. J. H. de Boer, Electron Emission and Adsorption Phenomena, Cambridge University Press, Cambridge 1935.

final step in the process comes the recombination of the atoms on the emergence surface and the desorption of the molecules formed, for which the activation energy E_d (fig. 6) is required.
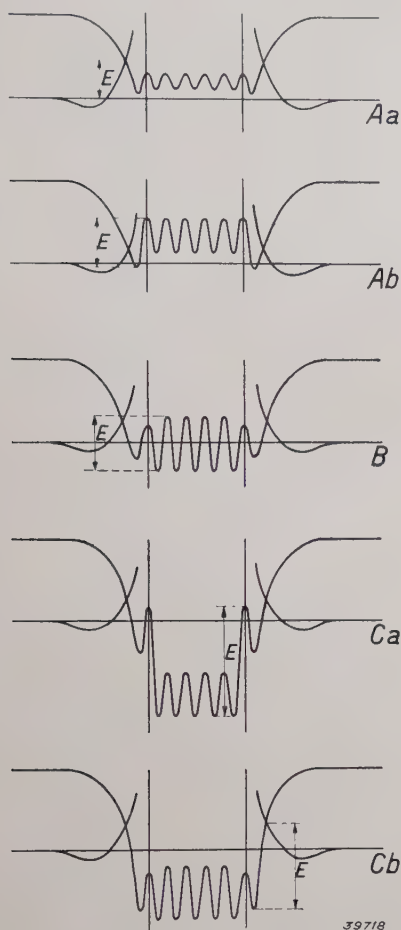

Fig. 7. Schematic representation by means of potential curves of the permeation of a gas through a thin metal wall. In *Aa* the dissociation of molecules into atoms on the entrance surface requires the greatest activation energy, in *Ab* the transition of the adsorbed atoms to the interior of the metal, in *B* the diffusion in the metal, in *Ca* the transition of the dissolved atoms to the emergence surface, in *Cb* the recombination of the adsorbed atoms on the emergence surface.

In principle of course it is possible to make the metal walls so thick that the diffusion process proper is the slowest of the various processes which occur in the permeation of gas. With not too thick walls,

such as are used in the experimental investigation and in technical problems, the following theoretical possibilities can be distinguished.

A) The rate of permeation is mainly determined by the reaction at the entrance surface. Two cases are then possible:
   a) The rate determining process is the transsition from van der Waals adsorption to activated adsorption, *i.e.* the dissociation of molecules into atoms (or ions) on the surface.
   b) The rate determining process is the transition of the atoms from the chemisorbed state to the inside of the entrance surface.

B) The rate of permeation is mainly determined by the diffusion in the interior of the metal.

C) The rate of permeation is mainly determined by the reaction at the emergence surface. There are again two possibilities:
   a) The rate determining process is the transition of the atoms from the inside of the emergence surface to the outside of this surface, *i.e.* the transition from the occluded to the chemisorbed state.
   b) The velocity determining process is the recombination of the adsorbed atoms.

These different possibilities are represented schematically by the composite potential curves of *fig.* 7. From the known facts it appears that all five types can be realized with different combinations of gas and metal and different conditions of the boundary surfaces. Examples of these five cases in order are the following:

Aa) hydrogen through an iron wall;
Ab) hydrogen through an iron wall with a very rough surface;
B) hydrogen through a copper wall;
Ca) oxygen through a zirconium wall;
Cb) oxygen through a copper or nickel wall.

In a later article in this periodical we hope to go into these and other examples of the permeation of gases through metal walls and the practical conclusions which may be drawn from them.

THE DETERMINATION OF THE ELASTIC CONSTANTS OF METALS

by M. J. DRUYVESTEYN.   620.172.225 : 621.317.755

The elastic constants of materials can be calculated from the characteristic frequencies of test rods in longitudinal and torsional vibration. In this article an arrangement is described with which these frequencies can be measured and with which measurements of the elastic constants of non-ferromagnetic metals were carried out. With the values of the constants found it is possible to check the isotropy of the substance. In certain cases large errors can be made if this check is omitted. This is explained in connection with the case of β-brass.

The modulus of elasticity E of a rod can be found by determining the elongation of the rod upon the extension of a tensile force P. E is given by the formula:

$$E = \frac{P}{d}\frac{l}{\Delta l}, \quad \cdots \cdots \quad (1)$$

where d is the diameter and l the length of the rod, while Δl is the elastic elongation caused by the tensile force. Plastic flow must not occur in this experiment and it is therefore necessary to keep $\Delta l/l$ very small; how small depends very much upon the material of the rod.

Since it is difficult to satisfy this condition and still attain great precision, in addition to the static method, Kundt (1865) already introduced a dynamic method of determining the modulus of elasticity. In the latter method the modulus of elasticity is calculated from the characteristic frequency of rods for longitudinal or for transverse vibrations [1]. In this case the relative changes in length may remain very small without detracting from the precision. The modulus of elasticity is connected with the characteristic frequency N_l of the longitudinal vibration of a cylindrical rod by the relation

$$E = \varrho \left(\frac{2}{n} N_l\, l \right)^2 \quad \cdots \cdots \quad (2)$$

In this expression ϱ is the density of the material and n a whole number which is 1 for the fundamental tone, 2 for the first overtone, etc.

From the transverse characteristic vibrations the modulus of elasticity can also be calculated. With a characteristic frequency N_{tr} of a square rod with the thickness a the following holds:

$$E = \varrho c \left(\frac{N_{tr}\, l^2}{a} \right)^2 \quad \cdots \cdots \quad (3)$$

c is here a constant which depends upon the order of the characteristic vibration and which has the value 0.947 for the fundamental tone.

Another elastic constant is the rigidity or modulus of shear Φ. We shall define this with the help of fig. 1 in which $ABCD$ represents the
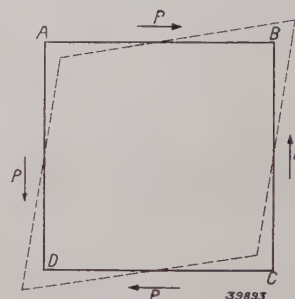

Fig. 1. Deformation of a cube by a shearing stress.

cross section of a cube of 1 cm³ of a given material. A force P acts along the upper surface, while along the other three surfaces BC, CD and DA forces also of the magnitude P act in the directions indicated. By these forces, which together form two opposite couples, the cube is deformed so that the cross section is now diamond-shaped with the angles $\pi/2-\varphi$ and $\pi/2+\varphi$. The rigidity Φ is then defined as P/φ.

The rigidity can also be determined by the measurement of the characteristic frequencies of elastic vibrations of a test rod. If N_t is the frequency of the torsional vibration (order n) of a circular rod, the following is true:

$$\Phi = \varrho \left(\frac{2}{n} N_t\, l \right)^2 \quad \cdots \cdots \quad (4)$$

The characteristic frequencies of the torsional vibrations in the case of a circular rod are thus independent of the diameter, as is the case for the longitudinal vibrations.

For the generation and measurement of the characteristic vibration electrical methods can now be used to advantage. We shall here describe an arrangement which was used in this labo-

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[1] In the static method the isothermal value of the elastic constants is found, in the dynamic method, the adiabatic value. The difference is slight (<1%) and can easily be calculated.

ratory and found suitable for the determination of the elastic constants of non-ferromagnetic metals. We shall then give several results which were obtained in measurements with this apparatus.

Method

We determined the elastic constants E and Φ of a number of non-ferromagnetic metals from the characteristic frequencies of the longitudinal and torsional vibration of the rods. We did not use the transverse vibration.

The rods were made to vibrate by placing them in the field of a permanent magnet and inducing alternating currents in the rods, whereupon the magnetic field exerts ponderomotive forces. *Fig. 2*
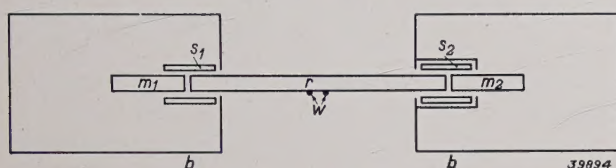

Fig. 2. Arrangement for the determination of the resonance frequency in the case of longitudinal vibrations. An alternating current of known frequency is sent through the coil s_1. Together with the inhomogeneous field of the magnet m_1 this current gives rise to longitudinal vibrations of the rod r. These vibrations, especially in the case of resonance, cause A.C. voltage in the coil s_2 which are observed with a cathode ray oscillograph.

is a diagram of the arrangement which was used for the excitation of the longitudinal vibration. The rod rests upon two thin metal wires w. Around the extremities of the rod are coils s_1 and s_2 and behind the rod the permanent magnets m_1 and m_2. Through coil s_1 flows an alternating current of variable and accurately known frequency which is generated by means of a tone generator. Eddy currents are induced in the rod r by these alternating currents. These eddy currents in the non-

homogeneous field of the permanent magnet give rise to longitudinal forces which alternate with the frequency of the eddy currents. The frequency of the alternating currents is now varied until it is equal to one of the longitudinal characteristic frequencies of the rod, so that resonance occurs in this vibration form.

This mechanical resonance can be ascertained with the help of a cathode ray oscillograph. For that purpose a coil s_2 and a magnet m_2 are placed at the other end of the rod, in an arrangement identical to that of s_1 and m_1 for the excitation of the vibration. Because of the longitudinal motion of the second extremity of the rod in the magnetic field, eddy currents are also excited in this end of the rod which induce in coil s_2 an A.C. voltage which is fed, *via* an amplifier, to one of the deflection systems of the cathode ray oscillograph.

The coils are surrounded by earthed copper boxes b, while the rod is also earthed in order to make the mutual induction of the coils as small as possible. *Fig. 3* shows a photograph of the arrangement used.

Fig. 4 is a diagram of the arrangement used for torsional vibration, with the shielding boxes emitted for the sake of simplicity. The currents induced in the rod by the coils s_1, with the help of the field of the magnet m_1 give rise to a couple on the rod as a result of which torsional vibration may occur. In this case also the arrangement for the ascertainment of the vibration is similar to that for its excitation.

In order to make the occurrence of the couple clear in fig. 4 the eddy currents and the magnetic lines of force are indicated by arrows. The ponderomotive force which is perpendicular to the direction of the current and of the lines of force, acts, at the moment illustrated, forward above the
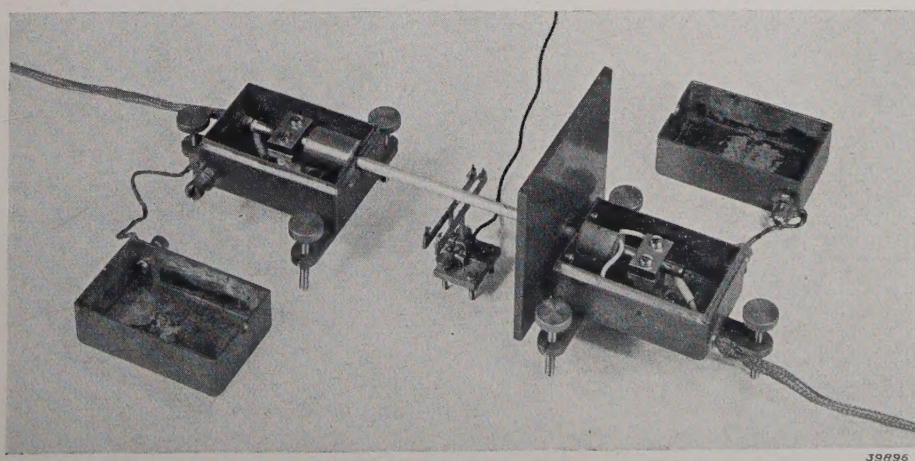

Fig. 3. Photograph of the arrangement represented in fig. 2.

axis of the rod and backward below the axis of the rod, so that a couple occurs in the direction of the arrow K. Due to the non-homogenity of the magnetic field the force directed toward the rear, which is excited close to the magnet, will be slightly larger than the force directed forward, so that in addition to the couple a tranverse force toward the rear is also exerted. In addition to the rotational vibrations therefore transverse vibrations may also be expected.
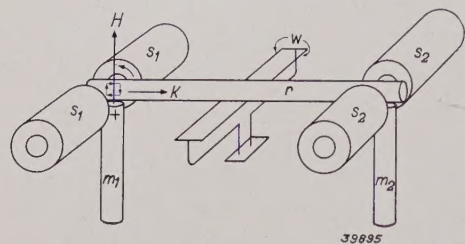

Fig. 4. Arrangement for the determination of the resonance frequency upon torsional vibrations; s_1, s_2 coils, m_1, m_2 magnets, w wires upon which the test rod r rests.

A possibility of ascertaining the vibrational form concerned consists in a comparison of the results, for rods of the same kind but of different diameter. The characteristic frequency of the transverse vibrations depends very closely upon the diameter, while that of torsional vibrations, as we have seen, is independent of the diameter. When the characteristic frequencies vary with the thickness of the rod, it may be concluded that one is not concerned with pure torsional vibrations.

Such a variation was actually found to occur when ferromagnetic rods were investigated. The fact that the transverse forces become especially large in this case is understandable in connection with the deformation of the magnetic field which the ferromagnetic rod causes. It was indeed found impossible to carry out reproducible elasticity measurements on these rods.

Several results

With the method described many characteristic frequencies could sometimes be measured. In the case of an aluminium rod for example, both for the longitudinal vibration and for the torsional vibration 8 overtones in addition to the fundamental tone could be measured. In the case of substances with less good electrical conduction and a greater internal damping than aluminium, sometimes only the fundamental could be measured.

In general the different overtones of a vibration furnish values of E as well as of Φ which agree very well among themselves and which are only slightly different for different test rods of the same

metal. This is, however, not always the case. Thus in an investigation of the elastic constants in the series of alloys of copper and zinc [2] remarkably divergent results were obtained in the case of one alloy, namely β-brass. The values found for E and Φ varied in a sometimes irreproducible way with the treatment which the rods had undergone. *Table I* gives an example of the results of several measurements. It was found that the chemical composition had only a slight effect on the elastic constants E and Φ and therefore that the differences which were found for the different rods, and which sometimes amount to 30 per cent or more, must be ascribed to other causes.

Table I

Modulus of elasticity E and rigidity Φ for β-brass (51-53% Cu, 49-47% Zn, sometimes 0.1% Cr) after different treatment.

Treatment	$E \cdot 10^{-11}$ dynes/cm²	$\Phi \cdot 10^{-11}$ dynes/cm²
not rolled	6·06	3·77
50% rolled at 700° C, annealed at 700°	6·54	3·43
30% rolled at 300° C, annealed at 500°	7·02	3·24
50% rolled at 500° C, annealed at 500°	9·46	3·52
8% rolled at 300° C, 30% rolled at 400° C, annealed at 450°	9·16	3·32

Explanation of the results

If the value of the modulus of elasticity is studied as it is measured by different authors for a given substance in polycrystalline state, it is striking that the differences which occur are considerably greater than could be explained by errors in measurement with the precision indicated, although they are seldom as great as in table I. These differences may be ascribed chiefly to poorly reproducible properties of the material used, such as:

1) impurities, deviations in the chemical composition,
2) cavities, cracks and similar material flaws,
3) anisotropy of the material.

As an example of 2) polycrystalline tungsten may be mentioned. The modulus of elasticity of drawn tungsten wires is found to depend upon their thickness, which may be ascribed to the fibrous structure of such wires. The cohesion in directions perpendicular to the wire is slight, so that in these directions the values found for the moduli of elasticity and the rigidity are too small.

Since the third point, anisotropy, may be very important for metals we shall go into it in somewhat

[2] M. J. Druyvesteyn and J. L. Meyering, Physica, 8, 1059, 1941.

more detail. A polycrystalline material is built up of a number of crystals. For most single crystals the modulus of elasticity depends very closely upon the direction in which it is measured. A polycrystalline material will only have a modulus of elasticity which is independent of the direction (*i.e.* will be elastically isotropic) when the crystals are distributed uniformly over all directions.

In the case of cast test rods this condition will sometimes be satisfied. It may, however, also happen that upon solidification of the liquid material a certain preferential direction of the crystallites becomes evident (so-called casting texture [3]). Upon working a metal, by hammering, forging or drawing, new textures may appear. In all these cases the elastic constants depend upon the state of working and on the direction in which the constants are measured; the scattering in the values of E and Φ which hereby occur may amount to more than 30 per cent.

The occurrence of a texture can also be ascertained by taking X-ray photographs of the substance. It is, however, also possible to ascertain the presence of preferential orientations from the elasticity measurements themselves. For this purpose, in addition to the moduli of elasticity and the rigidity, the compressibility K is also determined. K indicates the relative change in volume divided by the pressure from all sides necessary to produce it. Furthermore the Poisson constant μ must be determined (*i.e.* the relation between the relative lateral contraction to the relative elongation which occurs in stretching a rod).

For an isotropic homogeneous substance the following is valid:

$$K = \frac{9}{E} - \frac{3}{\Phi}, \qquad \mu = \frac{E}{2\Phi} - 1. \quad . \quad . \quad (5)$$

If E, Φ, K and μ are measured the correctness of these formulae can be checked and in this way it can be ascertained whether or not the material investigated was isotropic and homogeneous. Since

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[3]) Moreover in the case of cast material there is a relatively large chance of the occurrence of cavities.

[4]) E. Grüneisen, Ann. Physik **22**, 801, 1907.
    D. A. G. Bruggeman, dissertation, Utrecht 1930.

a slight change in E or Φ usually leads to a large change in the calculated values of μ and K, this is a very sensitive method.

β-brass

Since the elastic anisotropy of β-brass single crystals is abnormally great, a texture will in this case lead to great differences in the elastic constants E and Φ, so that the explanation of the differences occurring in table I becomes obvious. In *table II* in addition to the values of E and Φ from table I we also give the values calculated from those values according to equation (5) for K and μ. By direct measurements Bridgman found for the compressibility of β-brass a value of 9.1×10^{-13} dyne^{-1} cm^2, while the value of μ for every isotropic substance must lie between zero and 0.5, and usually lies between 0.15 and 0.45. On the basis of the values calculated for K and μ it may therefore be concluded that the test rods used for the first three substances were certainly not homogeneous and isotropic.

Table II

Modulus of elasticity E and rigidity Φ, together with the values calculated according to equation (5) of the compressibility K and the Poisson constant μ for β-brass.

$E \cdot 10^{-11}$	$\Phi \cdot 10^{-11}$	$K \cdot 10^{13}$	μ
Dynes/cm²	Dynes/cm²	Dynes^{-1} cm²	
6.06	3.77	70	—0.19
6.54	3.43	51	—0.05
7.02	3.24	35	0.09
9.46	3.52	9.9	0.34
9.16	3.32	7.5	0.38

In the last two measurements the calculated value of K does not deviate very much from the value measured by Bridgman and the calculated value of μ is not contradictory to the theoretically expected value. The elastic constants of the polycrystalline isotropic material must therefore be deduced from these measurements, so that it may be stated that the modulus of elasticity of β-brass probably lies between 9.0 and 9.5×10^{-11} dynes/cm².

ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS OF THE N.V. PHILIPS' GLOEILAMPENFABRIEKEN

An adequate number of reprints for the purpose of distribution is not available of those publications marked with an asterisk. Reprints of other publications may be obtained on application to the Natuurkundig Laboratorium, N.V. Philips' Gloeilampenfabrieken, Eindhoven (Holland), Kastanjelaan.

1554: E. J. W. Verwey: Energieën in de colloid-chemie (Energies in colloid chemistry) (Handelingen Ned. natuur- en geneesk. Congr., Apr. 1941, p. 88-90).

A survey is given in this lecture of the attempts to calculate the hydration and solvation energies of electrolytic solutions for positive and negative ions separately on the basis of the theory of Bernal and Fowler which has been somewhat improved by the author. These quantities are very important for boundary surface phenomena in colloid chemistry. The investigations will be published in detail in Rec. trav. chim. 1941.

1555: A. Bouwers: De biologische and medische toepassingen van kunstmatige radioactivi-teit (The biological and medical applications of artificial radioactivity) (Handelingen Ned. natuur- en geneesk. Congr., Apr. 1941, p. 207-211).

In this lecture before a combined meeting of physicists, biologists and medical men a survey was given of the method by which artificial radio active substances can now be prepared by means of transmutation of atomic nuclei (*cf.* Philips techn. Rev., **6**, 46, Feb. 1941). These substances have already been used with much success in biological and medical research. In order to measure the intensity of the radioactivity of a substance or in certain parts of the organism to be examined, the biologist or doctor can profitably use a simple electron counter which was demonstrated during the lecture and which is also described in detail in Philips techn. Rev. **6**, 75, Mar. 1941. In conclusion the favourable results were pointed out which have also already been obtained with artificial radio-activity in the field of therapy.

1556: L. Blok: Toestel voor het electrisch meten van de gehoorscherpte (Apparatus for the electrical measurement of the acuity of hearing) (Handelingen Ned. natuur- en geneesk. Congr., Apr. 1941, p. 212-214).

For the contents of this lecture before a combined meeting of physicists and doctors the reader may be referred to an article which has since appeared in Phil. techn. Rev. **6**, 234, Aug. 1941 on this audiometer.

1557: B. D. H. Tellegen: Phaenomenologie der piezo-electriciteit (The phenomena of piezo-electricity) (Ned. T. Natuurk. **8**, 270-274, July 1941).

In this opening address of the symposium on piezoelectricity organized by the Netherlands Physical Society and the Netherlands Radio Society (May 1941) a description is first given, on the basis of a one-dimensional image, of how the electrical polarization and the mechanical deformation of crystals may be connected. The equations are then derived thermodynamically which describe these piezoelectric phenomena, while finally it is indicated how these considerations must be extended in order to treat a three-dimensional case, such as actually occurs.

1558: J. de Boer: Toepassing van piezo-electri-sche kristallen bij geluidsweergave. (The application of piezoelectric crystals in sound reproduction). Ned. T. Natuurk. **8**, 345-356, July 1941).

In this address at the symposium on piezo-electricity (May 1941) the way is discussed in which mechanical vibrations can be converted into electrical A.C. voltages and the reverse with the help of crystals of Rochelle salt. The peculiar piezoelectrical properties of such crystals, such as the occurrence of two Curie temperatures, are discussed. Finally forms of construction for microphones and gramophone pick-ups with piezoelectric crystals are discussed (*cf.* also: Philips techn. Rev. **5**, 140, 1940).